CHEMISTRY today

India's #1 CHEMISTRY MONTHLY FOR JEE (Main & Advanced) & PMTs

Chemistry Musing

Olympiad Problems

AIIMS SPECIAL
Assertion & Reason
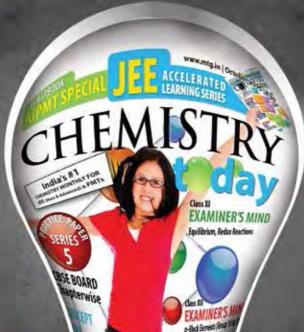
Advanced Chemistry Bloc

Concept Map

Concept Booster

ACE YOUR WAY CBSE PRACTICE PAPER

You Ask ❓
We Answer ✅

CHEMISTRY t👍day

Volume 25   No. 2   February 2016

CONTENTS

CHEMISTRY MUSING

PROBLEM
Set 31

JEE MAIN/PMTs

1. Which of the following diagrams is correctly related to the conductivity of complex under the same conditions in water?

(a)
$$CoCl_3 \cdot 6NH_3$$
Decrease — Decrease
$$CoCl_3 \cdot 4NH_3 \xleftarrow{Decrease} CoCl_3 \cdot 5NH_3$$

(b)
$$CoCl_3 \cdot 6NH_3$$
Increase — Decrease
$$CoCl_3 \cdot 4NH_3 \xleftarrow{Decrease} CoCl_3 \cdot 5NH_3$$

(c)
$$CoCl_3 \cdot 6NH_3$$
Decrease — Increase
$$CoCl_3 \cdot 4NH_3 \xleftarrow{Increase} CoCl_3 \cdot 5NH_3$$

(d)
$$CoCl_3 \cdot 6NH_3$$
Increase — Increase
$$CoCl_3 \cdot 4NH_3 \xleftarrow{Decrease} CoCl_3 \cdot 5NH_3$$
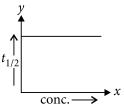
2. The plot of $t_{1/2}$ vs conc. of reactant is shown below :

The order of reaction is
(a) 0
(b) 1
(c) 2
(d) 3

3. What is the product Y in the following reaction sequence?

$$\xrightarrow[NH_{3(aq.)}]{Ag^+} X \xrightarrow[\Delta]{H^+} Y$$

(a)
(b)
(c)
(d)
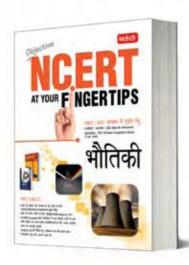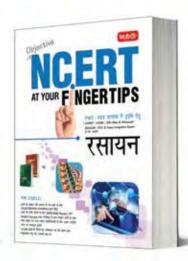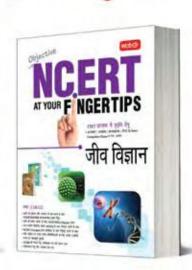
4. Oxygen is more electronegative than sulphur, yet H_2S is acidic while H_2O is neutral. This is because
(a) water is a highly associated compound
(b) H—S bond is a weaker than H — O bond
(c) H_2S is a gas while H_2O is a liquid
(d) the physical state of H_2O is liquid.

5. A pale green crystalline salt of metal 'M' dissolves freely in water. On standing, it gives a brown ppt. on addition of aqueous NaOH. The metal salt solution also gives a black ppt. on bubbling H_2S in basic medium. An aqueous solution of the metal salt decolourises the pink colour of the permanganate solution. 'M' is
   (a) copper   (b) aluminium
   (c) lead   (d) iron.

JEE ADVANCED

6. A solution contains Na_2CO_3 and $NaHCO_3$. 10 mL of the solution requires 2.5 mL of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as the indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M H_2SO_4 is required. The amount of Na_2CO_3 in g/L is
   (a) 5.3   (b) 4.2
   (c) 10.6   (d) 8.4

COMPREHENSION

C_7H_6O is the organic compound (A) which reacts with NaOH followed by acid hydrolysis to give two products (X) and (Y). (X) on oxidation gives (A) which on further oxidation gives (Y). Chloro derivative (Z) of (Y) is formed when (Y) is treated with PCl_5. The compound (Z) on reaction with NH_3 gives (D) which gives aniline on treatment with Br_2/KOH.

7. The compound 'D' is
   (a) benzoyl chloride   (b) benzamide
   (c) benzylamine   (d) benzonitrile.

8. The molecular weight of compound (X) is
   (a) 106 g mol^{-1} (b) 108 g mol^{-1}
   (c) 140.5 g mol^{-1} (d) 121g mol^{-1}

INTEGER VALUE

9. The moles of HCl that are required to prepare one litre of buffer solution (containing NaCN + HCl) of pH 8.5 using 0.01 g formula weight of NaCN ($K_{a(HCN)} = 4.1 \times 10^{-10}$) is 8.85×10^{-x}. The value of x is

10. Ethene is oxidised to glycol by cold alkaline $KMnO_4$ which is reduced to a new salt. The oxidation number of Mn in the salt is   ◈ ◈

AIPMT exam will go hi-tech to stop mass cheating replay

The Central Board of Secondary Education (CBSE) will be all geared up to ensure that no incident of mass cheating occurs during the All India Pre-Medical Entrance Test (AIPMT), to be conducted on May 1 next year.

The HRD ministry, in a meeting with the CBSE, has finalised a foolproof plan—which will include arming over 1,000 examination centres across the country with handheld metal detectors, mobile phone jammers and fingerprint scanners—to prevent a repeat of the entrance test's notorious 2015 episode.

The last medical entrance test, taken by over six lakh candidates, was cancelled and re-conducted on the Supreme Court's order when reports emerged of students at certain centres of Haryana indulging in mass-cheating by stitching Bluetooth devices and sophisticated microphones into their clothes.

While the metal detectors and jammers (to be used with the government's permission) will check the use of audio-visual devices, the use of fingerprint scanners will prevent the entry of fraudulent candidates into medical colleges.

"The applicants, at the time of making the application, will need to send scanned fingerprint impressions along with their photographs. At the centre, their fingerprint impressions will be collected again through inkless pads," an official told HT. This will ensure that the candidate who filled the application and the one who took the examination are the same, he added.

Considering that some students had earlier scanned their question papers and passed them to accomplices outside through sophisticated audio-visual devices, the CBSE has now decided to bar candidates from carrying phones, watches and even pens into the examination centre.

FOOLPROOF

- **Metal detectors, jammers to check use of two-way mics**
- **Fingerprint scanners to catch proxy applicants**
- **Video recording of the 3-hour exam at centres across India**
- **Cellphones, watches banned. Pens would be provided at the exam centre.**
- **Full-sleeved shirts, shoes not allowed**

"Although handheld metal detectors can discover such devices at the centre's entrance, invigilators will also be given flashlights to ensure candidates do not stuff tiny microphones into their vests or ears. We will be providing candidates with pens at the centre," the CBSE official said.

Voicing his approval for the CBSE's plan, former NCERT director and educationist JS Rajput said, "The CBSE has enough resources to make foolproof arrangements. Moreover, it collects over ₹1,000 from each candidate... Also, procuring metal detectors and fingerprint scanners for one day is a very much feasible solution. It should not be a problem."

However, not everybody seemed excited about the security arrangements being made. "Such elaborate arrangements could turn out to be a hassle for students, who will suffer for what some cheats did in the previous exam. I hope CBSE ensures that there is no chaos at the centres," Vaibhav Singh, a student, said.

Courtesy : Hindustan Times

PRACTICE PAPER
JEE MAIN & ADVANCED

*Dr. Sangeeta Khanna

CLASS-XI

SINGLE OPTION CORRECT

1. Air contains 21% of oxygen by volume. The number of moles of O_2 present in 5 L of air at STP conditions is
   (a) 2.23×10^{-1} (b) 4.68×10^{-4}
   (c) 4.68×10^{-2} (d) 0.0234

2. A sample of gas has a volume of V_1 litre at temperature $t_1°C$. When the temperature of the gas is changed to $t_2°C$ at constant pressure, then the volume of the gas was found to increase by 10%. The percentage increase in temperature is
   (a) 10%   (b) $\left(10 + \dfrac{2730}{t_1}\right)\%$
   (c) 20%   (d) $(0.1 + t_1^{-1})\%$

3. For three different gases, values of van der Waals' constant 'a' and 'b' are given. What is the correct order of liquefaction of gases?

Gas	'a'	'b'
X_2	1.3	0.090
Y_2	4.1	0.023
Z_2	2.2	0.075
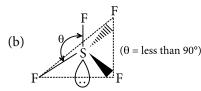
   (a) $X_2 > Y_2 > Z_2$ (b) $Y_2 > Z_2 > X_2$
   (c) $Z_2 > Y_2 > X_2$ (d) $X_2 > Z_2 > Y_2$
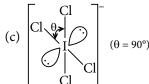
4. The ratio of average speed of an oxygen molecule to the *RMS* speed of a nitrogen molecule at the same temperature is
   (a) $\left(\dfrac{3\pi}{7}\right)^{1/2}$ (b) $\left(\dfrac{7}{3\pi}\right)^{1/2}$
   (c) $\left(\dfrac{3}{7\pi}\right)^{1/2}$ (d) $\left(\dfrac{7\pi}{3}\right)^{1/2}$
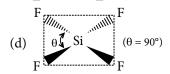
5. The liquefaction behaviour of temporary gases approaches that of permanent gases as we go
   (a) below critical temperature
   (b) above critical temperature
   (c) above absolute zero
   (d) below absolute zero.

6. The kinetic energy of 4 moles of nitrogen gas at $127°C$ is ($R = 2$ cal mol^{-1} K^{-1})
   (a) 4400 cal   (b) 3200 cal
   (c) 4800 cal   (d) 1524 cal

7. When the temperature is raised, viscosity of the liquid decreases. This is because
   (a) volume of the solution decreases
   (b) increase in temperature increases the average kinetic energy of the molecules which overcomes the attractive forces between them
   (c) covalent and hydrogen bond forces decreases
   (d) attraction between the molecule increases.

8. The pH of a solution prepared by mixing 2 M, 100 mL HCl and 1 M, 200 mL NaOH at $25°C$ is
   (a) 8   (b) 7
   (c) 4   (d) 5

9. Out of N_2O, SO_2, I_3^+, I_3^-, H_2O, NO_2^-, N_3^-, the linear species are
   (a) NO_2^-, I_3^+, H_2O (b) N_2O, I_3^+, N_3^-
   (c) N_2O, I_3^-, N_3^- (d) N_3^-, I_3^-, NO_2^-

10. In which of the following ionisation processes, the bond order has increased and the magnetic behaviour has changed?
    (a) $N_2 \longrightarrow N_2^+$ (b) $C_2 \longrightarrow C_2^+$
    (c) $NO \longrightarrow NO^+$ (d) $O_2 \longrightarrow O_2^+$

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11. In which of the following pairs, the hybridisation of central atoms is same, but geometry is not the same?
(a) SO_3, CO_3^{2-} (b) SO_3^{2-}, NH_3
(c) PCl_5, $POCl_3$ (d) XeF_2, ICl_3

12. Which of the following structure is correctly drawn according to fundamental idea of VSEPR theory?

(a) P, F, θ, F, F (θ = greater than 109°28′)

(b) S, F, F, F, θ (θ = less than 90°)

(c) $\begin{bmatrix} Cl, Cl, I, Cl, Cl, \theta \end{bmatrix}^-$ (θ = 90°)

(d) Si, F, F, F, F, θ (θ = 90°)
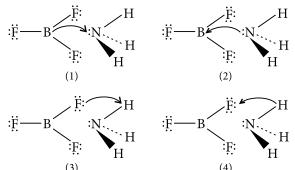
13. Select correct statement for BrF_5.
(a) All fluorine atoms are in same plane.
(b) Four fluorine atoms and Br atom is in same plane.
(c) Four fluorine atoms are in same plane.
(d) It has all F – Br – F bond angles at 90°.

14. Consider a p_y-orbital of an atom and identify correct statement.
(a) s-orbital of another atom produces π-bond when y is the bond formation axis.
(b) p_y-orbital of another atom produces σ-bond when x is the bond formation axis.
(c) p_z-orbital of another atom produces π-bond when x is the bond formation axis.
(d) d_{xy}-orbital of another atom produces π-bond when x is the bond formation axis.

15. Back bonding in BF_3 does not affect
(a) planarity, Lewis acidic strength and bond angle
(b) bond length, hybridisation and bond strength
(c) bond angle, planarity, geometry
(d) Lewis acidity, bond length, bond order (B – F).

16. Which of the following will have maximum dipole moment?

(a) (benzene ring)

(b) (benzene ring with three Cl at adjacent positions)

(c) (benzene ring with three Cl, Cl, Cl)

(d) (benzene ring with two Cl para positions)

17. Which of the following is not the consequence of H-bonding?
(a) Glycerol is more soluble in water than ethanol.
(b) Boiling point of C_2H_5OH is higher than CH_3—O—CH_3.
(c) p-nitrophenol has higher boiling point than o-nitrophenol.
(d) HCl is water soluble due to H-bonding.

18. BF_3 and NH_3 undergo a Lewis acid-base reaction forming an adduct. Which picture below correctly represents the curved arrow notation for the initial Lewis acid-Lewis base interaction in this reaction, what is the Lewis acid and the Lewis base?

(1)

(2)

(3)

(4)

(a) Picture (1) is correct; NH_3 is the Lewis acid and BF_3 is the Lewis base.
(b) Picture (2) is correct; BF_3 is the Lewis acid and NH_3 is the Lewis base.
(c) Picture (3) is correct; NH_3 is the Lewis acid and BF_3 is the Lewis base.
(d) Picture (4) is correct; BF_3 is the Lewis acid and NH_3 is the Lewis base.

19. The two equilibrium $AB \rightleftharpoons A^+ + B^-$ and $AB + B^- \rightleftharpoons AB_2^-$ are simultaneously maintained in a solution with equilibrium constant K_1 and K_2 respectively. The ratio of $[A^+]$ to $[AB_2^-]$ in the solution is
(a) directly proportional to the concentration of B^-
(b) inversely proportional to the concentration of B^-

(c) directly proportional to the square of the concentration of B^-

(d) inversely proportional to the square of the concentration of B^-.

20. Consider the following equilibrium in a closed container,
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
At a fixed temperature, the volume of the reaction container is halved. For this change which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?

(a) Neither K_p nor α changes.

(b) Both K_p and α change.

(c) K_p changes, but α does not change.

(d) K_p does not change, but α changes.

21. The degree of dissociation 'α' of the reaction :
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
can be related to K_p as :

(a) $\alpha = \dfrac{\dfrac{K_p}{P}}{4+\dfrac{K_p}{P}}$

(b) $\alpha = \dfrac{K_p}{4+K_p}$

(c) $\alpha = \left[\dfrac{K_p/P}{4+K_p/P}\right]^{1/2}$

(d) $\alpha = \left[\dfrac{K_p}{4+K_p}\right]^{1/2}$

22. Ammonium carbamate when heated to 200°C gives a mixture of NH_3 and CO_2 vapour with a density of 13. What is the degree of dissociation of ammonium carbamate?

(a) $\dfrac{3}{2}$ (b) $\dfrac{1}{2}$ (c) 2   (d) 1

23.

When A_2 and B_2 are allowed to react, the equilibrium constant of the reaction at 27°C is found ($K_c = 4$).
$$A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$$
What will be the equilibrium concentration of AB?

(a) 1.33 M   (b) 2.66 M

(c) 0.66 M   (d) 0.33 M

24. For the reaction,
$$A_{(g)} + 2B_{(g)} \rightleftharpoons 3C_{(g)} + D_{(g)}; K_p = 0.05 \text{ atm at 1000 K.}$$
The value of K_c is represented by

(a) $5 \times 10^{-4} R$

(b) $\dfrac{5 \times 10^{-4}}{R}$

(c) $5 \times 10^{-5} R$

(d) $\dfrac{5 \times 10^{-5}}{R}$

25. Consider the following reactions,

(i) $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

(ii) $CO_2 + H_2O \rightleftharpoons H_2CO_3$

(iii) $NH_3 + H_2O \rightleftharpoons NH_4OH$

(iv) $HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$
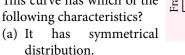
Which of the pairs of reaction proves that water is amphoteric in character?
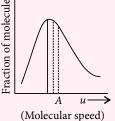
(a) (i) and (ii)   (b) (ii) and (iii)

(c) (iii) and (iv)   (d) (i) and (iii)

MORE THAN ONE OPTION CORRECT
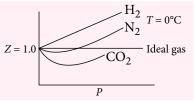
26. Which of the following statement(s) is/are true?

(a) HF is more polar than HBr.

(b) CuCl is more covalent than NaCl.

(c) HF is less polar than HBr.

(d) Chemical bond formation takes place when forces of attraction overcome the forces of repulsion.

27. The Maxwell-Boltzmann distribution law of molecular speeds is graphically represented as shown in the given figure.

This curve has which of the following characteristics?

(a) It has symmetrical distribution.
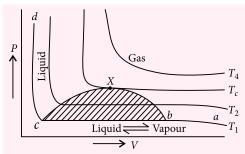
(b) The point A on X-axis represents the most probable speed.

(c) The area under the curve gives the total number of molecules.

(d) The maxima of the curve shifts to the right as the temperature increases.

28. Which of the following is/are correct statement(s) for compressibility factor?

(a) Z is always greater than 1 for H_2.

(b) For N_2, $Z < 1$ in the lower pressure region and $Z > 1$ in the higher pressure region. The curve has a minimum at particular pressure.

(c) In CO_2, Z dips sharply below the ideal line in the lower pressure region.

(d) Gases for which $Z > 1$ show positive deviation from ideal behaviour and for which $Z < 1$, shows negative deviation from ideal behaviour.

29. Which is/are correct for the graph for liquefaction of CO_2?

(a) At the point c, the liquefaction is complete and the curve cd represents the variation of V with P of the liquid state.
(b) The pressure corresponding to the line bc is known as the vapour pressure of the liquid.
(c) For every gas, there is a limit of temperature above which it cannot be liquefed, no matter what the pressure is.
(d) At temperature T_c, the horizontal pressure is reduced to a mere point. At temperature higher than T_c, there is liquefaction of gas.

CLASS-XII

SINGLE OPTION CORRECT

1. In the given reaction product 'P' is

(a)   (b)

(c)   (d)

2. $+ (CH_3CO)_2O \xrightarrow{H^+} X + CH_3COOH$

The compound 'X' is

(a)   (b)

(c)   (d)

3. End product of the following sequence of reaction is

 $\xrightarrow[\text{(ii) } H^+, \Delta]{\text{(i) } I_2 + NaOH, \text{ heat}}$

(a) CHI_3,

(b) CHI_3,

(c) CHI_3,

(d) CHI_3,
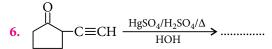
4. $\xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2 + KOH} B \xrightarrow{HONO} C$

The end product C is

(a)   (b)

(c)   (d)

5. $\xrightarrow[\text{(ii) } H_2O, \Delta]{\text{(i) } HNO_2} X \xrightarrow{NaOH} Y \xrightarrow{CH_3I} Z;$

Z is

(a)   (b)

(c)   (d)

6.

$$\xrightarrow[\text{HOH}]{\text{HgSO}_4/\text{H}_2\text{SO}_4/\Delta} \quad \text{.............}$$

The major product is

(a)

(b)

(c)

(d)

7.

 $\xrightarrow[\text{Zn/H}_2\text{O}]{\text{O}_3} X \xrightarrow{\text{KOH}/\Delta} Y$

The compound Y is

(a)

(b)

(c)

(d)

8.

 $\xrightarrow{\text{Zn-Hg/HCl}}$ Product

(a)

(b)

(c)

(d)

9.

$\xrightarrow{\text{H}_2/\text{Ni}/\Delta} A$

$\xrightarrow{\text{H}_2/\text{PtO}_2} B$

$\xrightarrow[\text{ether}]{\text{LiAlH}_4} C$

Here, A, B and C respectively are

(a)

(b) in all cases

(c) in all cases

(d)

10. The number of aldol reaction(s) that occurs in the given transformation is

$$\text{CH}_3\text{CHO} + 4\text{HCHO} \xrightarrow{\text{NaOH}}$$

 $+ \text{HCO}\overset{-}{\text{O}}\text{Na}^+$

(a) 1   (b) 2

(c) 3   (d) 4

11.

 $\xrightarrow[\text{(ii) H}_2\text{O/H}^+]{\text{(i) NaOH/373K}}$ ......

The major product is

(a)

(b)

(c)

(d)

12. Presence of two or three 'OH' groups on one C-atom causes unstability. Still, some such compounds are stable. Which of the following is stable?

(a) $\text{CCl}_3\cdot\text{CH(OH)}_2$

(b)

(c) (d) All of these

13. Acetone and its next Homologue are reacted with hydroxylamine under suitable conditions. The total number of organic products are
    (a) 2   (b) 3   (c) 4   (d) 5

14. The Cannizzaro reaction of a benzaldehyde involves an
    (a) intramolecular shift of proton
    (b) intermolecular shift of hydride
    (c) intermolecular shift of proton
    (d) intramolecular shift of hydride.

15. End product of the following sequence of reactions is

$$HC \equiv CH \xrightarrow{CH_3MgBr} HC \equiv CMgBr \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CO_2}$$

$$\xleftarrow[\Delta]{Ag_2O} \xleftarrow[HOH]{HgSO_4/H_2SO_4}$$

(a) $CH_3-\overset{\overset{O}{\|}}{C}-COOH$ (b) $CH_2(COOH)_2$

(c) $CH_3-\overset{\overset{O}{\|}}{C}-CHO$ (d) $H-\overset{\overset{O}{\|}}{C}-CH_2COOH$

16. $\xrightarrow{HCl/heat} A$

    Product (A) is

    (a)

    (b) $Ph-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-Ph$
    (c) $Ph-CH=CH-\underset{\underset{OH}{|}}{CH}-Ph$
    (d) $Ph-CH=C=CH-Ph$

17. $\xrightarrow{NBS} A \xrightarrow{aq.\ KOH} B$

    The main product (B) of the reaction is :

    (a)   (b)

    (c)   (d)

MORE THAN ONE OPTION CORRECT

18. Which of the following are incorrect order of acidic strength?

    (a)

    (b)

    (c)

    (d)

19. Which is/are correctly matched?
    (a) $RNH_2 + C_6H_5COCl \xrightarrow{NaOH}$
       $C_6H_5CONHR + HCl$
       : Schotten Baumann's Reaction
    (b) $CH_3CH_2COOH \xrightarrow{Cl_2}{P} CH_3-\underset{\underset{Cl}{|}}{CH}-COOH$
       : H.V.Z Reaction
    (c) $CH_3-CHO \xrightarrow[\Delta]{NaOH} CH_3-CH=CH-CHO$
       : Cannizzaro Reaction
    (d) $R-CONH_2 \xrightarrow{Br_2 +}{KOH} RNH_2$
       : Hoffmann Bromamide degradation

20. Which of the following reactions are correctly represented?
    (a) $CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{|}{Cl}}{C}}-CH_3 \xrightarrow[\text{(2) HOH, H}^+]{\text{(1) KCN}} CH_3-\underset{\underset{COOH}{|}}{CH}-CH_3$
       (3) Heating
    (b) $CH_3-CH_2-COOH \xrightarrow[\text{(2) } aq.\ KOH]{\text{(1) Br}_2,\ \text{small amount of phosphorus}}$
       Lactic acid($\pm$)

(c) $CH_3MgBr + $ $\xrightarrow[\text{hydrolysis}]{\text{followed by}} CH_3-CH-CH_3$
                                                                    $|$
                                                                    OH

(d) $CH_3-CH_2\overset{+}{O}\overset{-}{N}a + $ (benzene ring with COOH) $\rightarrow$ (benzene ring with COO$^-$Na$^+$) $+ CH_3CH_2OH$

21. Which of the following are correct statements?
(a) β-Ketoacids decarboxylate faster than α-keto acids.
(b) Succinic acid on heating will form cyclic anhydride.
(c) 2-Hydroxy butanoic acid on heating will form but-2-enoic acid.
(d) Benzoic acid is stronger acid than formic acid.

22. $CH_3-CH-COOH \xrightarrow{\Delta}$ Product
            $|$
            OH
      (±) Lactic acid

Which are correct for the products formed in this reaction?
(a) Products formed are stereoisomers.
(b) Three products are formed.
(c) *Cis*-isomer of product has a plane of symmetry.
(d) *Trans*-isomer of products has a centre of symmetry.

23. Which of the following compounds can form hydrazone and will give iodoform test but will not give Tollens' test?

(a) (cyclohexyl)$-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$

(b) $CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_2-CH_3$

(c) $CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_2-CHO$

(d) CH_3-CH_2-OH

24. $CH_3-CH=CH-CHO \xrightarrow{\text{Reagent}}$
$CH_3CH=CH-COOH$

Reagents used for this conversion will be
(a) Tollens' reagent
(b) 2, 4-dinitrophenyl hydrazine
(c) Benedict's reagent
(d) $KMnO_4$

25. Which of the following are arranged in correct order as indicated?

(a) (C$_6$H$_4$(CHO)(NO$_2$)) > (C$_6$H$_5$CHO) > (C$_6$H$_4$(CHO)(CH$_3$)) > (C$_6$H$_4$(CHO)(OCH$_3$))
[Nucleophilic addition reaction]

(b) $CH_3COCl > (CH_3CO)_2O > CH_3COOCH_3 > CH_3CO\ddot{N}H_2$
[Acyl S_N2 reaction]

(c) $CH_3CH_2COOH > CH_3COOH > HCOOH$
[Rate of esterification reaction]

(d) $CH_3COOCH_3 > CH_3COOC_2H_5 > CH_3COOC_3H_7$
[Rate of hydrolysis]

26. Which of the following compounds will give effervescence of N_2 with HNO_2 at 0 – 5°C?

(a) CH_3CONH_2 (b) (benzene ring with NH$_2$)

(c) $CH_3-CH-NH_2$ (d) (benzene ring)$-CONH_2$
         $|$
         CH_3

1. **(c) :** Volume of oxygen in 5 L of air $= \dfrac{5 \times 21}{100} L$

Number of moles (n) at STP $= \dfrac{V\,L}{22.4} = \dfrac{5 \times 21}{100 \times 22.4}$
$= 4.68 \times 10^{-2}$

2. **(b):** $V_2 = \left(V_1 + \dfrac{V_1 \times 10}{100}\right) = 1.1\,V_1$

Now, $\dfrac{V_1}{(t_1 + 273)} = \dfrac{1.1\,V_1}{(t_2 + 273)}$ or $t_2 = (1.1t_1 + 27.3)$

Increase in temperature $= 1.1t_1 + 27.3 - t_1$
$= (0.1t_1 + 27.3)$

Percent increase $= \dfrac{(0.1t_1 + 27.3) \times 100}{t_1}$
$= \left(10 + \dfrac{2730}{t_1}\right)\%$

3. **(b):** Higher the value of van der Waals' constant for attraction (a), easier is the liquefaction of gas.

4. (b): $u_{av}(O_2) = \sqrt{\dfrac{8RT}{\pi \times 32}}$

$u_{rms}(N_2) = \sqrt{\dfrac{3RT}{28}}$

$\therefore \quad \dfrac{u_{av}(O_2)}{u_{rms}(N_2)} = \sqrt{\dfrac{8 \times 28}{\pi \times 32 \times 3}} = \sqrt{\dfrac{7}{3\pi}}$

5. (b): Temporary gas cannot be liquefied above its critical temperature.

6. (c): $K.E = \dfrac{3}{2}nRT$

$= \dfrac{3}{2} \times (4\ mol) \times (2\ cal\ mol^{-1}\ K^{-1}) \times (400\ K)$

$= 4800\ cal$

7. (b)

8. (b): Millimoles of HCl and NaOH are equal.

9. (c): $^- :\overset{..}{N} = \overset{+}{N} = \overset{..}{N}:^-$, $^-N = \overset{+}{N} = O$, $[I-I-I]^-$

10. (c):

$\underset{\substack{B.O. = 2.5 \\ (Paramagnetic)}}{NO} \longrightarrow \underset{\substack{B.O. = 3 \\ (Diamagnetic)}}{\overset{+}{NO}}$

11. (d):

(Linear)   (T-shape)

12. (c): (a) θ = less than 109°28′
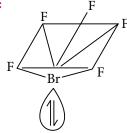
(b) Incorrect position of lone pair
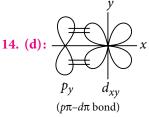
(c) Square planar structure with θ = 90°

(d) $\theta \neq 90°$ in SiF_4 because it is tetrahedral

13. (c):

14. (d):

$p\pi$ d_{xy}

($p\pi$–$d\pi$ bond)

15. (c): Geometry, planarity and F—B—F bond angles are not affected by back bonding in BF_3.

16. (b)   **17. (d)**   **18. (b)**

19. (d): $K_1 = \dfrac{[A^+][B^-]}{[AB]}$ and $K_2 = \dfrac{[AB_2^-]}{[AB][B^-]}$

$\therefore \quad \dfrac{K_1}{K_2} = \dfrac{[A^+][B^-]^2}{[AB_2^-]} \quad \therefore \quad \dfrac{[A^+]}{[AB_2^-]} \propto \dfrac{1}{[B^-]^2}$

20. (d)

21. (c): $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

$t_0 \qquad 1 \qquad\qquad 0$

$t_{eq} \qquad 1-\alpha \qquad 2\alpha$

$\sum n = 1 - \alpha + 2\alpha = 1 + \alpha$

$\Delta n_g = 2 - 1 = 1$

$K_p = \dfrac{(2\alpha)^2}{(1-\alpha)} \times \left(\dfrac{P}{1+\alpha}\right)^1$

$K_p = \dfrac{4\alpha^2}{1-\alpha^2}P$

$\alpha = \left[\dfrac{K_p/P}{4 + K_p/P}\right]^{1/2}$

22. (d): $NH_2 - COONH_4 \longrightarrow 2NH_{3(g)} + CO_{2(g)}$

$D = \dfrac{M_w}{2} = \dfrac{78}{2} = 39$

$\alpha = \dfrac{D-d}{(n-1)d} = \dfrac{39-13}{(3-1)13} = 1$

23. (c): $A_{2(g)} + B_{(g)} \rightleftharpoons 2AB_{(g)}$

$t_0 \qquad \dfrac{2}{4} \qquad \dfrac{4}{4} \qquad\qquad 0$

$t_{eq} \qquad \dfrac{2-x}{4} \qquad \dfrac{4-x}{4} \qquad \dfrac{2x}{4}$

$K_c = \dfrac{[AB]^2}{[A_2][B_2]}$

$4 = \dfrac{[2x/4]^2}{\left(\dfrac{2-x}{4}\right)\left(\dfrac{4-x}{4}\right)}$

$$4 = \frac{4x^2}{x^2 - 6x + 8}$$

$$x^2 - 6x + 8 = x^2$$

$$x = \frac{8}{6} = \frac{4}{3}$$

$$[AB] = \frac{2x}{4} = \frac{2}{4} \times \frac{4}{3} = 0.66 \text{ M}$$

24. (d): $K_c = \dfrac{K_p}{(RT)^{\Delta n}} = \dfrac{0.05}{(1000 \times R)^1} = \dfrac{5 \times 10^{-5}}{R}$

25. (c): In (iii), H_2O donates proton and in (iv), H_2O accepts proton.

26. (a, b, d) **27. (c, d)** **28. (a, b, c, d)**

29. (a, b, c)

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CLASS-XII

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1. (d): $H_3C-C=NMgBr$

2. (b): Acetylation of OH group by acetic anhydride.

3. (c): Iodoform reaction followed by decarboxylation.

4. (d):

5. (c): $X = $; $Y = $; $Z = $

6. (b):

7. (b):

8. (a): It is Clemmensen reduction. OH is also converted to Cl.

9. (d): H_2/Ni attacks both $C=C$ and $>C=O$.
H_2/Pt attacks $C=C$ only.
$LiAlH_4$ attacks $>C=O$ only.

10. (c):

11. (a): Follow Cannizzaro reaction on each benzene ring.

12. (d)

13. (b):

(Only one compound)

(Two compounds)

14. (b)

15. (b): $HC \equiv C-COOH$

Anti-Markovnikov addition

16. (a) :

17. (c)   **18. (a, c, d)**   **19. (a, b, d)**

20. (a, b, d) : (a)

$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3 \xrightarrow{KCN} CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CN}{|}}{C}}-CH_3 \xrightarrow[HF]{HOH}$$

$$CH_3-\underset{\underset{COOH}{|}}{C}-CH_3 \xleftarrow[\Delta]{-CO_2} CH_3-\underset{\underset{HOOC\quad COOH}{}}{C}-CH_3 \xleftarrow{}$$

(b) $CH_3-CH_2-COOH \xrightarrow[\text{Reaction}]{HVZ}$

$$CH_3-\underset{\underset{OH}{|}}{CH}-COOH \xleftarrow{aq.\ KOH} CH_3-\underset{\underset{Br}{|}}{CH}-COOH$$

(c) $CH_3MgBr + \triangle\!\!\!\overset{O}{} \xrightarrow{\text{Hydrolysis}} CH_3-CH_2-\underset{\underset{OH}{|}}{CH_2}$

(d) Acid-base reaction.

21. (a, b, c)

22. (a, b, d) : Product is

Cis(d + l), *trans* (meso)

23. (a, b) : It should be a methylketone.

24. (a, c)

25. (a, b, d) : (a) Electron withdrawing groups favour nucleophilic addition.

(b) Good leaving group favour the process.

(c) Smaller acids are more reactive.

(d) Small alkyl groups in ester favour hydrolysis.

26. (a, c, d): (b) will form diazonium salt.

◈ ◈

PRACTICE PAPER

AIPMT

2016
Exam date 1st May
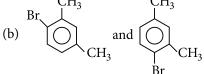
1. Which of the following diols would cleave into two fragments with HIO_4?
   (a) 1,3-Hexanediol   (b) 2,4-Hexanediol
   (c) 1,6-Hexanediol   (d) 3,4-Hexanediol

2. Artificial sweetener which is stable under cold conditions only is
   (a) saccharin   (b) sucralose
   (c) aspartame   (d) alitame.

3. (I) $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
   (II) $H_2O_2 + Ag_2O \longrightarrow 2Ag + H_2O + O_2$
   Role of hydrogen peroxide in the above reactions is respectively
   (a) oxidising in (I) and reducing in (II)
   (b) reducing in (I) and oxidising in (II)
   (c) reducing in (I) and (II)
   (d) oxidising in (I) and (II).

4. Which set of quantum numbers is possible for the last electron of Mg^+ ion?
   (a) $n = 3, l = 2, m = 0, s = +1/2$
   (b) $n = 2, l = 3, m = 0, s = +1/2$
   (c) $n = 1, l = 0, m = 0, s = +1/2$
   (d) $n = 3, l = 0, m = 0, s = +1/2$

5. Which of the following will have a *meso*-isomer?
   (a) 2-Chlorobutane
   (b) 2-Hydroxypropanoic acid
   (c) 2,3-Dichloropentane
   (d) 2,3-Dichlorobutane

6. Which of the following reactions is said to be entropy driven?
   (a) Endothermic reaction with positive entropy change and high temperature
   (b) Endothermic reaction with negative entropy change and low temperature
   (c) Exothermic reaction with positive entropy change and high temperature
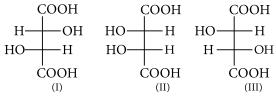
(d) Exothermic reaction with negative entropy change and low temperature

7. Which of the following does not liberate O_2 on heating?
   (a) MgO   (b) $NaNO_3$
   (c) Pb_3O_4 (d) $KClO_3$

8. If 10^{21} molecules are removed from 200 mg of CO_2, the number of moles of CO_2 left is
   (a) 2.88×10^{-3} (b) 28.8×10^{-3}
   (c) 0.288×10^{-3} (d) 1.66×10^{-2}

9. Leaving tendency of the following groups in decreasing order is

   I. Cl^- II. $CH_3-\bigcirc-SO_3^-$

   III. OH^- IV. $O_2N-\bigcirc-SO_3^-$

   (a) IV > II > I > III   (b) I > II > III > IV
   (c) II > IV > I > III   (d) I > IV > II > III.

10. What products are formed when the following compound is treated with Br_2 in the presence of $FeBr_3$?

(c)

and

(d) None of these

11. The ions O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+} are isoelectronic. Their ionic radii show
(a) a decrease from O^{2-} to F^- and then increase from Na^+ to Al^{3+}
(b) a significant increase from O^{2-} to Al^{3+}
(c) a significant decrease from O^{2-} to Al^{3+}
(d) an increase from O^{2-} to F^- and then decrease from Na^+ to Al^{3+}.

12. Acidity of diprotic acids in aqueous solutions increases in the order
(a) $H_2S < H_2Se < H_2Te$ (b) $H_2Se < H_2S < H_2Te$
(c) $H_2Te < H_2S < H_2Se$ (d) $H_2Se < H_2Te < H_2S$

13. The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is
(a) $RCOO^- < HC \equiv C^- < NH_2^- < R^-$
(b) $RCOO^- < HC \equiv C^- < R^- < NH_2^-$
(c) $R^- < HC \equiv C^- < RCOO^- < NH_2^-$
(d) $RCOO^- < NH_2^- < HC \equiv C^- < R^-$

14. The pH of 0.004 M hydrazine solution is 9.7. Its ionisation constant (K_b) is
(a) 7.79×10^{-8} (b) 4.49×10^{-9}
(c) 1.67×10^{-10} (d) 6.25×10^{-7}

15. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 300 K. The number of moles of NO_2 in 100 g of the mixture is approximately
(a) 0.44   (b) 4.4   (c) 33.4   (d) 3.34

16. Pair of enantiomers from the following compounds are

(a) I and II   (b) II and III
(c) I and III   (d) both (a) and (b).

17. In a face centred cubic arrangement of A and B atoms, A atoms are at the corners of the unit cell and B atoms at the face centres. One of the A atoms is missing from one corner in the unit cell. The simplest formula of the compound is
(a) A_7B_3 (b) AB_3
(c) A_7B_{24} (d) $A_{7/8}B_5$

18. Among the following mixtures, dipole-dipole as the major interaction is present in
(a) benzene and ethanol
(b) acetonitrile and acetone
(c) KCl and water
(d) benzene and carbon tetrachloride.

19. One mole of a complex compound $Co(NH_3)_5Cl_3$ gives 3 moles of ions when dissolved in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to form two moles of AgCl. The structure of complex is
(a) $[Co(NH_3)_5Cl]Cl_2$
(b) $[Co(NH_3)_3Cl_3].2NH_3$
(c) $[Co(NH_3)_4Cl_2]Cl.NH_3$
(d) none of these.

20. The energy absorbed by each molecule (A_2) of a substance is 4.4×10^{-19} J and bond energy per molecule is 4.0×10^{-19} J. The kinetic energy of the molecule per atom will be
(a) 2.2×10^{-19} J   (b) 2.0×10^{-19} J
(c) 4.0×10^{-20} J   (d) 2.0×10^{-20} J

21. An alkane C_7H_{16} is produced by the reaction of lithium di(3-pentyl)cuprate with ethyl bromide. The name of the product is
(a) 3-methylhexane   (b) 2-ethylpentane
(c) 3-ethylpentane   (d) *n*-heptane.

22. Thermal decomposition method is used to purify
(a) Ni   (b) Cr
(c) Sn   (d) Pb

23. Which of the following synthesis gives 3-methyl-1-hexanol?

(a) 2-Bromohexane $\xrightarrow[C_2H_5OC_2H_5]{Mg}$ $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } H_2C=O}$

(b) 2-Bromopentane $\xrightarrow[C_2H_5OC_2H_5]{Mg}$ $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } \triangle\!\!-\!\!O}$

(c) 3-Bromopentane $\xrightarrow[C_2H_5OC_2H_5]{Mg}$ $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3CH=O}$

(d) 1-Bromobutane $\xrightarrow[C_2H_5OC_2H_5]{Mg}$ $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3COCH_3}$

24. Which of the following are isoelectronic and isostructural?

NO_3^-, CO_3^{2-}, ClO_3^-, SO_3

(a) NO_3^-, ClO_3^-
(b) SO_3, NO_3^-
(c) CO_3^{2-}, SO_3
(d) Both (b) and (c)

25. The enthalpy of neutralisation of NH_4OH and CH_3COOH is -10.5 kcal mol^{-1} and enthalpy of neutralisation of CH_3COOH with strong base is -12.5 kcal mol^{-1}. The enthalpy of ionisation of NH_4OH will be
(a) 4.0 kcal mol^{-1}
(b) 3.0 kcal mol^{-1}
(c) 2.0 kcal mol^{-1}
(d) 3.2 kcal mol^{-1}

26. Which of the following is not the characteristic of interhalogen compounds?
(a) They are more reactive than halogens.
(b) They are quite unstable but none of them is explosive.
(c) They are covalent in nature.
(d) They have low boiling points and are highly volatile.

27. The product of acid hydrolysis of P and Q can be distinguished by

$$H_2C = \overset{OCOCH_3}{\underset{CH_3}{<}} \quad \underset{P}{} \qquad H_3C \diagdown \diagup \diagdown_{OCOCH_3} \quad \underset{Q}{}$$

(a) Lucas reagent
(b) 2,4-DNP
(c) Fehling's solution
(d) $NaHSO_3$

28. Which of the following orders is true regarding the basic nature of NH_2 group?
(a) *o*-Toluidine > Aniline > *o*-Nitroaniline
(b) *o*-Toluidine < Aniline > *o*-Nitroaniline
(c) *o*-Toluidine < Aniline < *o*-Nitroaniline
(d) *o*-Toluidine > Aniline < *o*-Nitroaniline

29. Schottky defect in crystals is observed when
(a) unequal number of cations and anions are missing from the lattice
(b) equal number of cations and anions are missing from the lattice
(c) anion leaves its normal site and occupies an interstitial site
(d) density of the crystal is increased.

30. The indicator that is obtained by coupling the diazonium salt of sulphanilic acid with *N,N*-dimethylaniline is
(a) phenanthroline
(b) methyl orange
(c) methyl red
(d) phenolphthalein.

31. Aqueous ammonia is used as a precipitating reagent for Al^{3+} ions as $Al(OH)_3$ rather than aqueous $NaOH$, because
(a) NH_4^+ is a weak base
(b) $NaOH$ is a very strong base
(c) $NaOH$ forms $[Al(OH)_4]^-$ ions
(d) $NaOH$ forms $[Al(OH)_2]^+$ ions.

32. The electronic configuration of actinoids cannot be assigned with degree of certainty because of
(a) small energy difference between $5f$ and $6d$ levels
(b) overlapping of inner orbitals
(c) free movement of electrons over all the orbitals
(d) none of the above.

33. If a solution containing components A and B follows Raoult's law then
(a) A—B attraction force is greater than A—A and B—B
(b) A—B attraction force is less than A—A and B—B
(c) A—B attraction force remains same as A—A and B—B
(d) volume of solution is different from sum of volumes of solute and solvent.

34. Fructose gives the silver mirror test because it
(a) contains an aldehyde group
(b) contains a keto group
(c) undergoes rearrangement under the alkaline conditions of the reagent to form a mixture of glucose and mannose
(d) none of these.

35. What happens when the temperature of a solution is increased from 25°C to 65°C ?
(a) The rate of the reaction remains unchanged and the rate constant k decreases.
(b) The rate of the reaction increases and rate constant k decreases.
(c) The rate of the reaction decreases and so does the rate constant k.
(d) The rate of the reaction increases and so does the rate constant k.

36. When $LiNO_3$ is heated, it gives oxide, Li_2O, whereas other alkali metal nitrates decompose to give corresponding
(a) nitrite
(b) peroxide
(c) both nitrite and oxide
(d) none of these.

37. End product of the following conversion is

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_2-CO_2H \xrightarrow[\text{(ii) } H_2O,\, H^+]{\text{(i) } NaBH_4}$$

(a)

(b)

(c)

(d) $H_3C-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2-CH_2-CO_2H$

38. A compound containing two –OH groups attached with one carbon atom is unstable but which one of the following is stable?

(a) $CH_3CH\begin{smallmatrix}OH\\OH\end{smallmatrix}$

(b) $CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-OH$

(c) $Cl_3C-CH\begin{smallmatrix}OH\\OH\end{smallmatrix}$

(d) None of these

39. Which one of the following statements is not true?
(a) pH of drinking water should be between 5.5 – 9.5.
(b) Concentration of DO below 6 ppm is good for the growth of fish.
(c) Clean water would have a BOD value of less than 5 ppm.
(d) Oxides of sulphur, nitrogen and carbon are the most widespread air pollutants.

40. Beckmann rearrangement is involved in the synthesis of which of the following polymers?
(a) PAN
(b) Nylon 6,10
(c) Nylon-6
(d) Melamine

41. Propanal on treatment with dilute sodium hydroxide forms
(a) $CH_3CH_2CH_2CH_2CH_2CHO$
(b) $CH_3CH_2CH(OH)CH_2CH_2CHO$
(c) $CH_3CH_2CH(OH)CH(CH_3)CHO$
(d) CH_3CH_2COONa

42. An explosion takes place when conc. H_2SO_4 is added to $KMnO_4$. Which of the following is formed?
(a) Mn_2O_7
(b) MnO_2
(c) $MnSO_4$
(d) Mn_2O_3

43. Which one of the following shows highest magnetic moment?
(a) V^{3+}
(b) Cr^{3+}
(c) Fe^{3+}
(d) Co^{3+}

44. $R-OH + HX \quad RX + H_2O$
In the above reaction, the reactivity of alcohols is
(a) tertiary > secondary > primary
(b) tertiary < secondary < primary
(c) tertiary > primary > secondary
(d) secondary > primary > tertiary

45. Which of the following is the least reactive compound towards nucleophilic acyl substitution?
(a) CH_3COCl
(b) $CH_3CONHCH_3$
(c) $CH_3CONHC_6H_5$
(d) $CH_3CONH-\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!-NO_2$

SOLUTIONS

1. (d): $CH_3-CH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2-CH_3 \xrightarrow{HIO_4}$
$2CH_3-CH_2-CHO$

2. (c): Aspartame is stable under cold conditions but unstable at cooking temperature.

3. (c):

Increase in oxidation state(reducing agent)

$\overset{-1}{H_2O_2} + O_3 \longrightarrow H_2O + \overset{0}{2O_2}$

Increase in oxidation state(reducing agent)

$\overset{-1}{H_2O_2} + \overset{+1}{Ag_2O} \longrightarrow 2\overset{0}{Ag} + H_2O + \overset{0}{O_2}$

Decrease in oxidation state

H_2O_2 acts as reducing agent in all those reactions in which O_2 is evolved.

4. (d): Last electron of Mg^+ is $3s^1$.
$Mg : 1s^2 2s^2 2p^6 3s^2$; $Mg^+ : 1s^2 2s^2 2p^6 3s^1$
∴ For an e^- in $3s$-orbital, the quantum numbers would be : $n = 3, l = 0, m = 0, s = +1/2$.

5. (d): 2,3-dichlorobutane contains a plane of symmetry $i.e.$, the upper half of the molecule is the mirror image of the lower half. The rotation of one half of the molecule will therefore exactly counter balance the rotation of other half, causing the molecule to be optically inactive. Such an internally compensated molecule is said to be a $meso$-form.

6. **(a) :** For endothermic reaction, ΔH = +ve. For reaction to be spontaneous, ΔS must be positive and also $T\Delta S$ must be greater than ΔH in magnitude. The reaction is then said to be entropy driven.

7. **(a) :** $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$

    $2Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2$

    $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

    MgO being high melting oxide does not decompose on heating to liberate O_2.

8. **(a) :** 200 mg CO_2 = 0.2 g $= \dfrac{0.2}{44} mol$ = 0.00454 mol

    $= 4.54 \times 10^{-3} mol$

    10^{21} molecules of $CO_2 = \dfrac{10^{21}}{6.02 \times 10^{23}} = 1.66 \times 10^{-3} mol$

    $\therefore$ No. of moles left $= (4.54 - 1.66) \times 10^{-3}$

    $= 2.88 \times 10^{-3}$

9. **(a) :** As the negative charge of leaving group can be delocalised into the phenyl ring and if additionally attached group on the ring has $-I$ effect it will further delocalise the negative charge then such group has higher leaving tendency. Thus the leaving group activity order is so.

10. **(b):** $-CH_3$ group is *o,p*-directing. Because of crowding, no substitution occurs at the carbon atom between the two $-CH_3$ groups in *m*-xylene, even though two $-CH_3$ groups activate that position.

1,3-Dimethylbenzene (*m*-Xylene)

11. **(c) :** Ionic radii of isoelectronic ions decrease with increase of nuclear charge thus, it shows a decrease from O^{2-} to Al^{3+}.

12. **(a) :** As the atomic size increases down the group, the bond length increases and the bond strength decreases and the cleavage of E–H (E = S, Se, Te) bond becomes easier thus, more will be the acidity. Hence, the correct order is : $H_2S < H_2Se < H_2Te$.

13. **(a) :** The order of basicity can be explained on the basis of the acidity of the acids of the given conjugate bases. Stronger the acid, weaker is the conjugate base. Since $RCOOH$ is the strongest acid amongst all, $RCOO^-$ is the weakest base. Due to *sp* hybridised carbon, acetylene is also acidic and hence, a weak base but stronger than $RCOO^-$.

As sp^3 carbon is less electronegative than sp^3 nitrogen, R^- is more basic than NH_2^-. So, the correct order is $RCOO^- < HC \equiv C^- < NH_2^- < R^-$.

14. **(d):** For weak bases :

    $[OH^-] = \sqrt{K_b \times C}$

    pH = 9.7 thus, pOH = 14 – 9.7 = 4.3

    $-\log[OH^-] = 4.3$

    $\Rightarrow [OH^-] = 5 \times 10^{-5}$

    $5 \times 10^{-5} = \sqrt{K_b \times 0.004}$

    or $K_b \times 0.004 = 25 \times 10^{-10}$

    $\Rightarrow K_b = \dfrac{25}{4 \times 10^{-3}} \times 10^{-10} = 6.25 \times 10^{-7}$

15. **(a) :** Molecular weight of the mixture = 38.3 × 2

    = 76.6

    Let mass of NO_2 in the mixture = *x* g
    then mass of N_2O_4 = (100 − *x*) g
    Number of moles of NO_2 = *x*/46

    Number of moles of $N_2O_4 = \dfrac{100 - x}{92}$

    (Molecular weight of NO_2 = 46, Molecular weight of N_2O_4 = 92)

    $\dfrac{Weight}{Number\ of\ moles} = Molecular\ weight$

    $\dfrac{x + (100 - x)}{\dfrac{x}{46} + \dfrac{(100 - x)}{92}} = 76.6 \Rightarrow \dfrac{x}{46} + \dfrac{(100 - x)}{92} = \dfrac{100}{76.6}$

    $x = 20.1$

    Number of moles of $NO_2 = \dfrac{20.1}{46} = 0.437 \approx 0.44$

16. **(c) :** Structures I and III are non-superimposable mirror images of each other. Hence, they are pair of enantiomers.

17. **(c) :** One atom of (*A*) is missing from one corner.

    No. of atoms *A* in unit cell $= 7 \times \dfrac{1}{8} = \dfrac{7}{8}$

    No. of atoms *B* in unit cell $= 6 \times \dfrac{1}{2} = 3$

    $A : B = \dfrac{7}{8} : 3$ so, simplest formula is A_7B_{24}.

18. **(b):** Dipole-dipole interactions occur among the polar molecules having permanent dipoles. The polarity of the molecules depends upon the electronegativities of the atoms present in the molecule and the geometry of the molecule.

Molecules	Interactions
Benzene and ethanol	Dispersion forces
Acetonitrile and acetone	Dipole-dipole
KCl and water	Ion-dipole
Benzene and CCl_4	Dispersion forces

19. (a) : Since the complex gives two moles of AgCl, there must be two ionisable chlorine atoms. Hence, compound should be $[Co(NH_3)_5Cl]Cl_2$.

$[Co(NH_3)_5Cl]Cl_2 + 2AgNO_3 \longrightarrow$
$\qquad\qquad [Co(NH_3)_5Cl](NO_3)_2 + 2AgCl\downarrow$

$[Co(NH_3)_5Cl]Cl_2 \rightleftharpoons \underbrace{[Co(NH_3)_5Cl]^{2+} + 2Cl^-}_{\text{Three ions}}$

20. (d) : Energy absorbed by each molecule $= 4.4 \times 10^{-19}$ J
Energy required to break the bond $= 4.0 \times 10^{-19}$ J
Remaining energy gets converted to kinetic energy
$\qquad = (4.4 \times 10^{-19} - 4.0 \times 10^{-19})$ J
$\qquad = 0.4 \times 10^{-19}$ J per molecule
$\therefore$ Kinetic energy per atom $= 0.2 \times 10^{-19}$ J
$\qquad = 2 \times 10^{-20}$ J

21. (c) :

$$(CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{\overset{\displaystyle CH_2}{\displaystyle |}}}}{CH-})_2CuLi + C_2H_5Br \longrightarrow$$

$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{\overset{\displaystyle CH_2}{\displaystyle |}}}}{CH}-C_2H_5 + CH_3-CH_2-\overset{\overset{\displaystyle |}{\overset{\displaystyle CH_2}{\overset{\displaystyle |}{\displaystyle CH_3}}}}{CH}-Cu + LiBr$

3-Ethylpentane

22. (a) : Ni combines with CO at 323 K to form $Ni(CO)_4$ which decomposes thermally at 423 K to give pure Ni metal.

$Ni(CO)_4 \xrightarrow{\text{423 K}} Ni + 4CO\uparrow$

23. (b) : $CH_3-CH_2-CH_2-\overset{\overset{\displaystyle |}{\displaystyle Br}}{CH}-CH_3$

$\downarrow$ Mg / Diethyl ether

$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle |}{\displaystyle MgBr}}{CH}-CH_3$

$\downarrow$ $\overset{CH_2-CH_2}{\underset{O}{\diagdown\diagup}}$

$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle |}{\displaystyle CH_3}}{CH}-CH_2-CH_2OMgBr$

$\downarrow$ H_3O^+

$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle |}{\displaystyle CH_3}}{CH}-CH_2-CH_2OH$

3-Methyl-1-hexanol
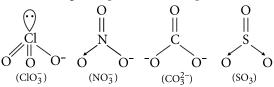
24. (d) : Total number of electrons in NO_3^-
$\qquad = (7 + 3 \times 8 + 1) = 32$
Total number of electrons in CO_3^{2-}
$\qquad = (6 + 3 \times 8 + 2) = 32$

Total number of electrons in ClO_3^-
$\qquad = (17 + 3 \times 8 + 1) = 42$
Total number of electrons in SO_3
$\qquad = (16 + 3 \times 8) = 40$
Therefore, NO_3^- and CO_3^{2-} are isoelectronic.
Structures of given species can be represented as :

Thus, NO_3^- and CO_3^{2-} are isostructural and isoelectronic.

25. (c) : ΔH_{neut} for a strong acid with a strong base
$\qquad = -13.7$ kcal equiv^{-1}
$\qquad = -13.7$ kcal mol^{-1}
$\qquad$ (For monovalent acids and bases)
$\Delta H_{\text{ion}}(CH_3COOH) = -12.5 - (-13.7)$
$\qquad = +1.2$ kcal mol^{-1}
$\Delta H_{\text{ion}}(NH_4OH) = -10.5 - (-13.7) - \Delta H_{\text{ion}}(CH_3COOH)$
$\qquad = 13.7 - 10.5 - 1.2 = 2$ kcal mol^{-1}

26. (d) : Some interhalogens are solids and are not volatile.

27. (c) :

28. (b) : *Ortho* substituted anilines are weaker bases than anilines regardless of the nature of the substituent whether electron releasing or electron withdrawing. This is called *ortho* effect and is probably due to a combination of steric and electronic factors.
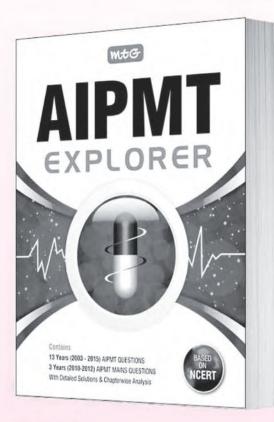
29. (b) : In Schottky defect, equal number of cations and anions are missing from the lattice.

30. (b):

Diazonium salt of sulphanilic acid + N,N-Dimethylaniline

$-HCl$

Methyl orange

31. (c): $Al(OH)_3$ formed with NaOH dissolves in excess of NaOH to form aluminate ion.

$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3\downarrow + 3NaCl$

$Al(OH)_3 + OH^- \longrightarrow [Al(OH)_4]^-$
 Soluble

32. (a): For the first four actinide elements, Th, Pa, U and Np, the difference in energy between $5f$ and $6d$-orbitals is small. Thus, in these elements (and their ions) electrons may occupy the $5f$ or the $6d$ levels or sometimes both. Later in the actinide series the $5f$-orbitals become appreciably lower in energy. Thus, from Pu onwards the $5f$-shell fills in a regular way.

33. (c): Raoult's law is valid for ideal solutions only. A solution containing components of A and B behaves as an ideal solution when A—B attraction force remains same as A—A and B—B.

34. (c): Under alkaline conditions of the reagent, fructose gets converted into a mixture of glucose and mannose (Lobry de Bruyn - van Ekenstein rearrangement) both of which contain the –CHO group and hence, reduce Tollens' reagent to give silver mirror test.

35. (d): With the increase of temperature, rate of reaction increases and thus rate constant also increases because rate $\propto$ rate constant.

36. (a): When $LiNO_3$ is heated it gives oxide, NO_2 and O_2 while other nitrates of alkali metals give oxygen and nitrites.

$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

$2MNO_3 \rightarrow 2MNO_2 + O_2$ (All Alkali metals except Li)

37. (a):

38. (c): Chloral hydrate is stable due to hydrogen bonding.

39. (b): Fishes die in water bodies having low level of dissolved oxygen (DO).

40. (c):

Cyclohexane $\xrightarrow{[O]}$ Cyclohexanol $\xrightarrow{[O]}$ Cyclohexanone

NH_2OH, $-H_2O$ → Cyclohexanone oxime $\xrightarrow[\text{rearrangement}]{\substack{H_2SO_4 \\ \text{Beckmann}}}$ Caprolactum $\xrightarrow{260-270°C}$

$\{C-(CH_2)_5-NH\}_n$
Nylon–6

41. (c): $CH_3CH_2CHO + CH_2=CHO$ (with CH_3 branch) $\xrightarrow[\text{condensation}]{\substack{NaOH \\ \text{Aldol}}}$

$CH_3CH_2CH-CHCHO$ (with OH and CH_3 branches)

42. (a): $2KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + Mn_2O_7 + H_2O$
(Conc.) (Explosive)

43. (c): Greater the number of unpaired electrons more will be the magnetic moment.

Ion	V^{3+}	Cr^{3+}	Fe^{3+}	Co^{3+}
Outer electronic configuration	$3d^2$	$3d^3$	$3d^5$	$3d^6$
No. of unpaired d-electrons	2	3	5	4

44. (a): Reactions of alcohols involving cleavage of C – OH bond follow the reactivity order :
Tertiary > secondary > primary, according to the stability of carbocation intermediate.

45. (b): More basic the leaving group, less reactive is the acyl derivative. Now basicity of the leaving groups decreases in the order :
$CH_3NH^- > C_6H_5NH^- > p\text{-}NO_2-C_6H_4-NH^- > Cl^-$,
therefore, $CH_3CONHCH_3$ is the least reactive acyl derivative. ◈◈

Y?U ASK
WE ANSWER

Q 1. **Explain the following :**

(a) What is horn silver and what are its uses?

(b) Which is the real metal among pnictogens?

(*Saswata Guchhait, West Bengal*)

Ans. (a) Horn silver is silver chloride, $AgCl$. It is a white crystalline solid having low solubility in water. On heating, $AgCl$ decomposes to metallic silver. It has a face-centred cubic lattice where each Ag^+ ion is surrounded by an octahedron of 6 Cl^- ligands.

Mineral form of $AgCl$ is chlorargyrite.

Horn silver is used as a reference electrode in photography as an antidote for mercury poisoning, as an antimicrobial agent for long term preservation of drinking water, in bandages and wound healing products and in the production of inglaze lustre in pottery.

(b) A pnictogen group, located in column 15 of the periodic table, also called nitrogen family. The group consists of elements nitrogen, phosphorus, arsenic, antimony, bismuth and Uup. Each member of the group contains five valence electrons and they form stable compounds. Binary compounds of these elements are called phictides. The real metal among pnictogens is bismuth. Nitrogen and phosphorus are non-metals while arsenic and antimony are metalloids.

Q 2. **Though —CH_3 is an *ortho/para* directing group, on alkylation it gives *meta* product. How?**

(*Ketki J. Desai, Gujarat*)

Ans. Alkylation of an aromatic compound is an electrophilic aromatic substitution reaction. As, —CH_3 group is an electron releasing group thus, it activates the benzene ring and gives electrophilic substitution reaction more easily than benzene. Now, due to its electron releasing nature, —CH_3 group increases electron density at *ortho* and *para*-positions of benzene ring. Thus, the incoming electrophile attacks at these positions to give *ortho/para* products

However, when the reaction is carried out at high temperature then the thermodynamically more stable product will be formed. In case of xylene, the *meta*-product is more stable when toluene reacts with methanol at temperature above 500°C.
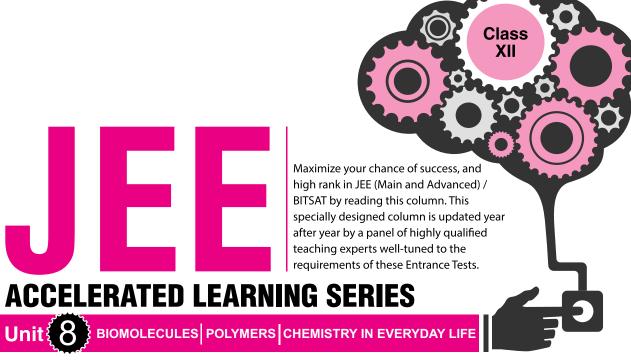
(Thermodynamic composition)

Q 3. **Why does the reaction rate of an enzyme - catalysed reaction change from first-order to zero-order as the substrate concentration is increased.**

(*Akil Sharma, Panipat*)

Ans. Each enzyme molecule has one or more 'active sites' at which the substrate must bind so that the catalytic action may occur. At low substrate concentration, most of these active sites remain unoccupied at any time. As the substrate concentration is increased, the number of active sites which are occupied increases and hence, the reaction rate also increases. However, at very high substrate concentration, virtually all the active sites are occupied at any time so that further increase in substrate concentration cannot further increase the formation of enzyme-substrate complex.

◈ ◈

JEE

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Unit 8 — BIOMOLECULES | POLYMERS | CHEMISTRY IN EVERYDAY LIFE

BIOMOLECULES
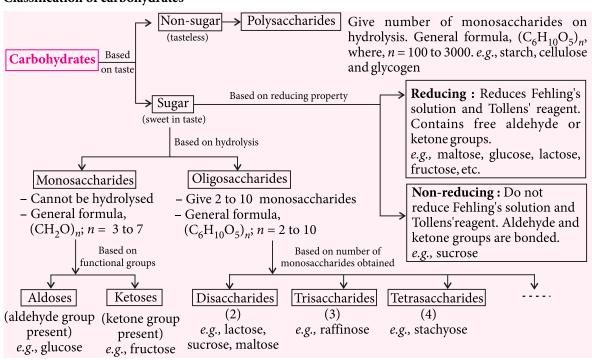
- Carbohydrates
- Proteins
- Vitamins
- Nucleic Acids

❑ **Classification of carbohydrates**

TIPS TO REMEMBER

Carbohydrates

❑ Carbohydrates are optically active polyhydroxy aldehydes or polyhydroxy ketones or substances which yield such products on hydrolysis. These are also known as *saccharides*.

Carbohydrates — Based on taste

→ Non-sugar (tasteless) → Polysaccharides

Give number of monosaccharides on hydrolysis. General formula, $(C_6H_{10}O_5)_n$, where, $n = 100$ to 3000. *e.g.*, starch, cellulose and glycogen

→ Sugar (sweet in taste) — Based on reducing property →

Reducing : Reduces Fehling's solution and Tollens' reagent. Contains free aldehyde or ketone groups.
e.g., maltose, glucose, lactose, fructose, etc.

Non-reducing : Do not reduce Fehling's solution and Tollens' reagent. Aldehyde and ketone groups are bonded.
e.g., sucrose

Based on hydrolysis:

Monosaccharides
– Cannot be hydrolysed
– General formula, $(CH_2O)_n$; $n = 3$ to 7

Based on functional groups:

Aldoses (aldehyde group present) *e.g.*, glucose

Ketoses (ketone group present) *e.g.*, fructose

Oligosaccharides
– Give 2 to 10 monosaccharides
– General formula, $(C_6H_{10}O_5)_n$; $n = 2$ to 10

Based on number of monosaccharides obtained:

Disaccharides (2) *e.g.*, lactose, sucrose, maltose

Trisaccharides (3) *e.g.*, raffinose

Tetrasaccharides (4) *e.g.*, stachyose

- - - - -

Monosaccharides

❑ Monosaccharides are the simplest carbohydrates which cannot be hydrolysed to smaller molecules.

❑ All monosaccharides are reducing sugars, *e.g.*, glucose, fructose, galactose (hexose) and ribose, arabinose (pentose).

❑ **Glucose :** Glucose or dextrose ($C_6H_{12}O_6$) has six carbon atoms including an aldehyde group hence, it is categorised as aldohexose.

  ○ *Preparation* :
   — *Laboratory method* : From sucrose (cane sugar)
   $$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
   $$\text{Sucrose} \qquad\qquad \text{Glucose} \quad \text{Fructose}$$
   — *Commercial method* : From starch
   $$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\text{393 K, 2-3 atm}]{H^+/\Delta} nC_6H_{12}O_6$$
   $$\text{Starch or Cellulose} \qquad\qquad \text{Glucose}$$
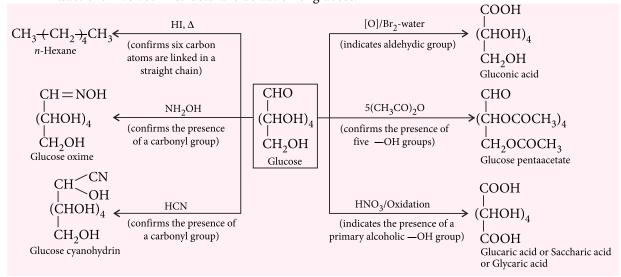
  ○ *Structure* : In open chain structure of glucose, there are four dissimilar chiral carbon atoms (C-2, C-3, C-4 and C-5) thus, 16 stereoisomeric forms are possible.

α-*D*-(+)-Glucopyranose   *D*-(+)-Glucose   β-*D*-(+)-Glucopyranose
(Cyclic structure)   (Open chain structure)   (Cyclic structure)

  ○ *Chemical Properties* :
   — Reactions involved in structural elucidation of glucose.
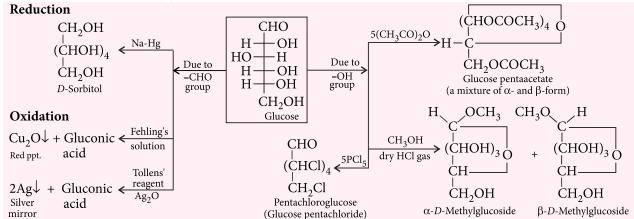
— The cyclic structure of glucose is represented by *Haworth structure*.

α-*D*-(+)-Glucopyranose   β-*D*-(+)-Glucopyranose

— α - and β-*D*-glucose have different configuration at anomeric (C-1) carbon atom, hence are called *anomers* and the C-1 carbon atom is called *anomeric carbon* (glycosidic carbon).

— α - anomer is less stable and constitutes 36% whereas β-anomer is more stable and constitutes 64% of the equilibrium mixture.

— An aqueous solution of glucose shows *mutarotation*, *i.e.*, its specific rotation gradually decreases from +110° to +52.5° in case of α-glucose and increases from +19.7° to +52.5° in case of β-glucose.

  ○ *Behaviour due to cyclic structure of glucose* :
   — Despite having the aldehyde group, it does not give 2,4-DNP test, Schiff's test and it does not form the hydrogensulphite addition product with $NaHSO_3$.
   — The pentaacetate of it does not react with hydroxylamine indicating the absence of free —CHO group in glucose pentaacetate.

– *Other reactions of glucose* :

Reduction

D-Sorbitol

Oxidation

$Cu_2O\downarrow$ + Gluconic acid
Red ppt.   ⟵ Fehling's solution

$2Ag\downarrow$ + Gluconic acid
Silver mirror   ⟵ Tollens' reagent Ag_2O

Glucose

Due to –CHO group

Due to –OH group

$5(CH_3CO)_2O$ → Glucose pentaacetate (a mixture of α- and β-form)

$5PCl_5$ ⟵ Pentachloroglucose (Glucose pentachloride)

CH_3OH dry HCl gas → α-D-Methylglucoside + β-D-Methylglucoside

– *Action of dilute alkalies* : Glucose on treatment with dilute alkali undergoes reversible isomerisation.
This rearrangement is known as *Lobry de Bruyn van Ekenstein rearrangement.*

D-(+)-Glucose   1,2-Enolization   Enediol

D-(+)-Mannose   D-(–)-Fructose

– *Action of concentrated alkalies* : Glucose on treatment with concentrated alkali turns yellow then brown and finally a brown-resinous mass.

❑ **Fructose** : Fructose or fruit sugar ($C_6H_{12}O_6$) has six carbon atoms including a ketonic group hence, it is categorised as ketohexose.

❑ Naturally occurring fructose is laevorotatory hence it is also known as *laevulose*.

○ *Preparation* :

– *Hydrolysis of cane sugar* :

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\Delta]{dil.\ H_2SO_4} C_6H_{12}O_6 + C_6H_{12}O_6$$
Cane sugar (Dextrorotatory)   D-Glucose (Dextrorotatory)   D-Fructose (Laevorotatory)

Fructose rotations are stronger than glucose rotations, thus the final mixture is found to be laevorotatory. As the rotation changes to laevorotatory from dextrorotatory, thus the solution is known as *invert sugar* and the process as *inversion*.

– *Hydrolysis of insulin* :

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{dil.\ H_2SO_4} nC_6H_{12}O_6$$
Insulin   Fructose

○ *Structure* :

– Its open chain structure is shown as follows :

D-(–)-Fructose

– It also exists in two cyclic forms which are obtained by the addition of —OH at C-5 to the ($> C = O$) group. The ring, thus formed is a five membered ring and is named as *furanose*.

α-D-(–)-Fructofuranose   β-D-(–)-Fructofuranose

– The cyclic structures of two anomers of fructose are represented by Haworth structures.

α-D-(–)-Fructofuranose   β-D-(–)-Fructofuranose

○ Fructose also undergoes mutarotation as shown :

α-D-Fructose ⇌ Equilibrium ⇌ β-D-Fructose
mixture

$[\alpha]_D = -21°$ $[\alpha]_D = -92°$ $[\alpha]_D = -133°$

❑ **Comparison of glucose and fructose**

Property	Glucose	Fructose
Molecular formula	$C_6H_{12}O_6$	$C_6H_{12}O_6$
Nature	Polyhydroxy aldehyde	Polyhydroxy ketone
Optical activity of natural form	Dextrorotatory	Laevorotatory
Oxidation		
(a) with bromine water (b) with conc. nitric acid	Gluconic acid Saccharic acid (glucaric acid)	No reaction Mixture of glycollic acid, tartaric acid and trihydroxyglutaric acid
Reduction with $NaBH_4$ or $Na\text{-}Hg/H_2O$	D-Sorbitol	Mixture of D-sorbitol and D-mannitol
Fehling's solution	Gives red precipitate	Gives red precipitate
Tollens' reagent	Forms silver mirror	Forms silver mirror
Resorcinol + HCl (dil.) (Selivanoff's test)	No colouration	Gives red or brown colour or precipitate
Freshly prepared ammonium molybdate sol. + few drops of acetic acid (Pinoff's test)	Light blue colour	Bluish green colour on heating
Alcoholic α-naphthol + HCl (conc.) (Furfural test)	No colouration	A purple colour (violet) on boiling
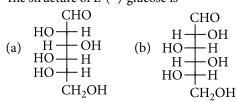
① KEY POINT
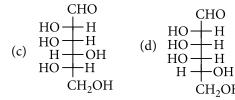
- All the naturally occurring monosaccharides have the –OH group at their penultimate carbon atoms towards right thus they belong of D-series.
- Excessive fructose consumption encourages ectopic fat deposition which may increase the risk of cardiovascular disease.

✓ SELF CHECK

1. The structure of D-(+)-glucose is

CHO
H——OH
HO——H
H——OH
H——OH
CH₂OH

The structure of L-(–)-glucose is

(a)
CHO
HO——H
H——OH
HO——H
HO——H
CH₂OH

(b)
CHO
H——OH
HO——H
H——OH
HO——H
CH₂OH

(c)
CHO
HO——H
HO——H
H——OH
HO——H
CH₂OH

(d)
CHO
HO——H
HO——H
HO——H
H——OH
CH₂OH

(JEE Advanced 2015)

2. Accumulation of which of the following molecules in the muscles occurs as a result of vigorous exercise?

(a) Glucose   (b) Glycogen
(c) L-Lactic acid   (d) Pyruvic acid

(JEE Main 2015)

3. The following carbohydrate is

(a) a ketohexose   (b) an aldohexose
(c) an α-furanose   (d) an α-pyranose

(IIT JEE 2011)

4. The two functional groups present in a typical carbohydrate are
   (a) $-OH$ and $-COOH$
   (b) $-CHO$ and $-COOH$
   (c) $>C=O$ and $-OH$
   (d) $-OH$ and $-CHO$ (AIEEE 2009)

Oligosaccharides

❑ These are the carbohydrates that yield two to ten monosaccharide units on hydrolysis. Oligosaccharides are further classified as disaccharides, trisaccharides, tetrasaccharides, etc. on the basis of number of monosaccharide units obtained on their hydrolysis.

　○ Disaccharides : In disaccharides, the two monosaccharide units are joined together by an oxide linkage formed by the loss of a water molecule, this linkage is known as *glycosidic linkage*. *e.g.*,

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
　　Sucrose　　　　　　　*D*-(+)-Glucose　*D*-(–)-Fructose

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} 2 \text{ moles of } \alpha\text{-}D\text{-glucose}$$
　　Maltose

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \beta\text{-}D\text{-Galactose}$$
　Lactose　　　　　　　　　$+ \beta$-*D*-Glucose
　(Milk sugar)
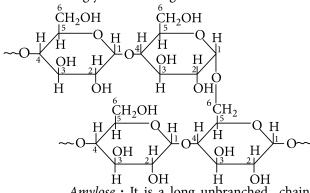
　　— *Structures of disaccharides* :
　　　➢ *Sucrose,* $C_{12}H_{22}O_{11}$ (*Cane sugar)*

(Glucose unit)　(Fructose unit)

　　　➢ *Maltose*, $C_{12}H_{22}O_{11}$ (*Malt sugar)*

(Reducing unit)　(Non-reducing unit)

　➢ *Lactose* ($C_{12}H_{22}O_{11}$) (*Milk sugar)*

(Glucose unit)　(Galactose unit)

Polysaccharides
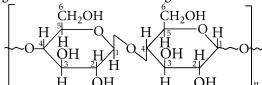
❑ Carbohydrates which yield a large number of monosaccharides on hydrolysis are called polysaccharides. *e.g.*, starch, cellulose, glycogen, gums, etc.

❑ They are non-reducing in nature due to absence of free aldehydic or ketonic group.

❑ **Starch $(C_6H_{10}O_5)_n$:**

　○ Starch occurs as reserved food material mainly in seeds, fruits and also in the roots of plants. The chief commercial sources of starch are wheat, maize, rice, potatoes, etc.

　○ It is a mixture of two components, a water insoluble component called *amylopectin* (80%) and a water soluble component called *amylose* (20%).

　　— *Amylopectin* **:** It is highly branched polysaccharide composed of chains of α-*D*-(+)-glucose units joined by α-glycosidic linkages.

　　— *Amylose* **:** It is a long unbranched chain of α-*D*-(+)-glucose units joined by α-glycosidic linkages.

- **Cellulose $(C_6H_{10}O_5)_n$:**
  - Cellulose is found in all plants and so is the most abundant of all carbohydrates.
  - It is a linear condensation polymer of β-D-glucose units which are joined by β-glycosidic linkages between C-1 of one glucose unit and C-4 of next glucose unit.

  - It dissolves in ammoniacal copper hydroxide solution (Schweitzer's reagent) but cellulose does not reduce Tollens' reagent or Fehling's solution. It does not form osazone and is not fermented by yeast.

- **Glycogen $(C_6H_{10}O_5)_n$:**
  - Glycogen is a condensation polymer of α-D-glucose.
  - It is the reserve carbohydrate of the animals and is stored in liver and muscles. At the time of requirement, it gets hydrolysed into glucose which on oxidation provides energy to the body.
  - Glycogen neither reduces Fehling's solution nor forms an osazone.

🔑 KEY POINT

- Sucrose does not have free aldehyde or ketone group which is shown by the facts that it does not form osazone, does not show mutarotation and does not exist in anomeric forms.
- Molisch's test is used for detection of all types of carbohydrates. In this test, 1% alc. solution of α-naphthol is added to aqueous solution of carbohydrate followed by conc. H_2SO_4. The violet ring at the junction of two layers is formed.
- Cellulose is not digestible to humans because human digestive system does not contain enzyme cellulase which can hydrolyse cellulose into glucose.

✓ SELF CHECK

5. Complete hydrolysis of starch gives
   (a) glucose and fructose in equimolar amounts
   (b) galactose and fructose in equimolar amounts
   (c) glucose only
   (d) glucose and galactose in equimolar amounts.
   (JEE Main 2015)

6. Which of the following compounds can be detected by Molisch's test?
   (a) Sugars   (b) Amines
   (c) Primary alcohols (d) Nitro compounds
   (AIEEE 2012)

7. The correct statement about the following disaccharide is

   (a) Ring (i) is pyranose with α-glycosidic link
   (b) Ring (i) is furanose with α-glycosidic link
   (c) Ring (ii) is furanose with α-glycosidic link
   (d) Ring (ii) is pyranose with β-glycosidic link
   (IIT JEE 2010)

Proteins
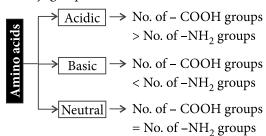
- Proteins are condensation polymers of α-amino acids *i.e.*, the compounds which have both the acid and amino group attached to the same carbon atom. The total number of amino acids that have been found in proteins are twenty.

$$R \overset{\alpha}{\underset{H}{-}C-} COOH \quad (R = \text{side chain})$$

α-Amino acid

- **Classification of amino acids :**
  - *On the basis of relative number of amino and carboxyl groups* :

    Amino acids
    - Acidic → No. of – COOH groups > No. of –NH_2 groups
    - Basic → No. of – COOH groups < No. of –NH_2 groups
    - Neutral → No. of – COOH groups = No. of –NH_2 groups

  - *On the basis of their synthesis* :
    - *Essential amino acids :* The amino acids which cannot be synthesised in the body and must be obtained through diet. *e.g.*, valine, leucine, lysine, isoleucine, arginine, etc.
    - *Non-essential amino acids :* The amino acids which can be synthesised in the body. *e.g.*, glycine, alanine, glutamic acid, aspartic acid, etc.

Name of amino acid	Structure of R	Three letter symbol
Glycine	–H	Gly
Alanine	$-CH_3$	Ala
*Valine	$-CH(CH_3)_2$	Val
*Leucine	$-CH_2CH(CH_3)_2$	Leu
*Isoleucine	$-CH-CH_2-CH_3$ $\quad\ \ |$ $\quad\ \ CH_3$	Ile
*Arginine	$-(CH_2)_3NH-\underset{\underset{NH}{\|\|}}{C}-NH_2$	Arg
*Lysine	$-(CH_2)_4NH_2$	Lys
Glutamic acid	$-CH_2CH_2COOH$	Glu
Aspartic acid	$-CH_2COOH$	Asp
Glutamine	$-CH_2CH_2CONH_2$	Gln
Asparagine	$-CH_2CONH_2$	Asn
*Threonine	$-CH(OH)CH_3$	Thr
Serine	$-CH_2OH$	Ser
Cysteine	$-CH_2SH$	Cys
*Methionine	$-CH_2CH_2SCH_3$	Met
*Phenylalanine	$-CH_2C_6H_5$	Phe
Tyrosine	$-CH_2C_6H_4OH(p)$	Tyr
*Tryptophan	$-CH_2$ (indole ring, HN)	Trp
*Histidine	$-CH_2$ (imidazole ring, NH, N)	His
Proline	(pyrrolidine ring, HN, COOH, H)	Pro
*Essential amino acids		

□ **Properties of amino acids :**

○ In aqueous solution the carboxylic group can lose a proton and amino group can accept a proton giving rise to a dipolar ion known as *zwitter ion*. This is neutral but contains both positive and negative charges.

$$R-\underset{:NH_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons R-\underset{\overset{+}{N}H_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^-$$

○ They form salts with acids as well as with bases, due to amine and carboxylic group. Thus, they are amphoteric substances and the phenomenon is known as *amphoterism*.

○ The equilibria are expressed as follows :

$$R-\underset{\overset{+}{N}H_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^- \underset{\underset{H^+}{\longleftarrow}}{\overset{H^+}{\overset{OH^-}{\rightleftharpoons}}} \begin{array}{l} R-CH-C \overset{O}{<}_{OH} \\ \quad |\ \ _{\overset{+}{N}H_3} \\ \text{amino acid in acidic solution} \end{array}$$

amino acid in alkaline solution

○ *Isoelectric point :* The pH at which dipolar ion (zwitter ion) exists as neutral ion, *i.e.*, +ve and –ve charge is equal and it does not migrate to either electrode, is called *isoelectric point*. The amino acids have least solubility in water at isoelectric point which helps in their separation.

○ *Optical activity of amino acids* : All amino acids except glycine are optically active because they contain chiral, asymmetric carbon atom. They exist in both *D* and *L*-forms. Most naturally occurring amino acids have *L*-configuration.

□ **Formation of proteins (peptide bond) :** The bond formed between two amino acids by the elimination of a water molecule is called a *peptide linkage or bond.*

$$-\underset{O}{\overset{\|}{C}}-\boxed{OH\ +\ H}-\underset{H}{\overset{}{N}}-\xrightarrow{-H_2O} -\underset{\underset{\underset{\text{peptide bond}}{}}{O\quad H}}{\overset{\|}{C}-\overset{|}{N}}-$$

□ Peptides are further divided into di, tri, tetra depending upon the number of amino acids combined.

$$H_2N-\underset{R}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}+\left[NH-\underset{R'}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}\right]_n NH-\underset{R''}{\underset{|}{CH}}-COOH$$

N-terminal amino acid → , ← C-terminal amino acid

R, R', R'' may be same or different.

□ A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 u is called a *protein*.

❑ **Structure of proteins :**
  ○ *Primary structure :* Primary structure refers to number and linear sequence of amino acids held together by peptide bonds.
    − Amino acid with free amino group forms one end of the chain and amino acid with free carbonyl group forms the other end.

Primary structure

  ○ *Secondary structure :* The conformation or shape which the polypeptide chain of a protein molecule acquire due to the secondary bondings such as hydrogen bonding between the carbonyl and amino groups, is called secondary structure of protein.
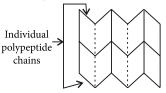
Secondary structure

α-helix β-pleated sheet

This is formed when the chain of α-amino acids coils as a right handed screw. Hydrogen bonding is responsible for holding helix in position. Such proteins are elastic.

Polypeptide chains are arranged side by side in a zig-zag manner. Neighbouring peptide chains are bonded together by inter-molecular H-bonds. In those cases, where *R* groups are smaller.

e.g., myosin (nucleus), keratin (hair), etc.

Individual polypeptide chains

e.g., silk protein (fibroin)

  ○ *Tertiary structure :* This arises due to folding and superimposition of various secondary structural elements.
    These are of two types :

Tertiary structure

Fibrous Globular
Linear polymers held by intermolucular H-Bond.
e.g., α-keratin, myosin, collagen, etc.

These are cross-linked proteins and have 3D folded structure.
e.g., insulin, pepsin, haemoglobin, etc.

  ○ *Quaternary structure :* Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these sub-units with respect to each other is known as quaternary structure of proteins.

❑ **Denaturation of proteins :** Breaking of hydrogen bonds either by acids or alcohols or heat, results in unfolding of globules. Thus, helix gets uncoiled and protein loses its biological activity due to change in temperature or pH. This is called denaturation of proteins.

Enzymes

❑ Enzymes are proteins produced by living systems and catalyse specific biological reactions.
The important enzymes are :

Enzymes	Reaction catalysed
Urease	Urea $\rightarrow CO_2 + NH_3$
Invertase	Sucrose $\rightarrow$ Glucose + Fructose
Amylase	Starch $\rightarrow n \times$ Glucose
Trypsin	Polypeptides$\rightarrow$ α-Amino acids
Nuclease	DNA, RNA $\rightarrow$ Nucleotides
Lactase	Lactose $\rightarrow$ Glucose + Galactose
Emulsin	Cellulose $\rightarrow n \times$ Glucose

❑ **Properties of enzymes :**
  ○ Enzymes are needed in very small amount.
  ○ They reduce magnitude of activation energy *e.g.,* E_a for hydrolysis of sucrose is 6.22 kJ/mol while in presence of sucrase, it reduces to 2.15 kJ/mol.
  ○ They are highly specific *i.e.,* they catalyse a particular reaction only.
  ○ They work at specific pH *e.g.,* salivary amylase becomes inactive in stomach due to acidic pH.
  ○ They work well at moderate temperature *e.g.,* milk is changed into curd at moderate temperature.
  ○ The non-proteinaceous part present in a protein is called *prosthetic group*.
    − The prosthetic group is necessary for proteins to act as enzyme and is known as *co-enzyme*. They may be defined as a substance necessary for the activity of enzymes. These are generally metal ions or small organic molecules.

❑ **Mechanism of enzyme catalysed reactions :**
The various steps involved in the enzyme catalysed reactions are given as follows.

○ Binding of the enzyme (*E*) to substrate (*S*) to form a complex.
$$E + S \longrightarrow ES$$

○ *ES* is called the enzyme-substrate complex.

○ Product formation in the complex.
$$ES \longrightarrow EP$$
where, *EP* is a complex of enzyme and product.

○ Release of product from the enzyme-product complex.
$$EP \longrightarrow E + P$$

🔑 KEY POINT

- Sanger's method is used to determined the N-terminal amino acid residue.
- Hydrazinolysis is the method used to determine the C-terminal amino acid residue.
- Ninhydrin (2,2-dihydroxyindane-1,3-dione) gives purple colouration with α-amino acids. This is known as *ninhydrin test* for identification of α-amino acids.

Vitamins

❑ A vitamin is a nutrient, an organic compound that is required in tiny amounts for essential metabolic reactions in a living organism. They cannot be made by the organisms and so have to be supplied in the diet. They are chemically different from other main nutrients *i.e.,* carbohydrates, proteins and fats. Their deficiency causes many diseases. There are about 25 vitamins known. They are broadly divided into two categories :

○ *Fat soluble vitamins* : Vitamin-A, D, E and K.

○ *Water soluble vitamins* : Vitamin-B_1, B_2, B_6, B_{12} and C.

Vitamin name	Chemical name	Solubility	Sources	Deficiency disease
Vitamin A	Retinoids (retinol and carotenoids)	Fat	Milk, butter, egg, fish, cod liver oil, green vegetables, etc.	Night-blindness, xerophthalmia
Vitamin B_1	Thiamine	Water	Pulses, nuts, cereals (rice, wheat, etc.), rice bran, yeast, egg yolk, fruits and green vegetables, etc.	Beri-beri, loss of appetite
Vitamin B_2	Riboflavin	Water	Milk, green vegetables, egg white, meat, liver, kidney, etc.	Anaemia, inflammation of tongue, dermatitis, cheilosis
Vitamin B_6	Pyridoxine	Water	Rice bran, whole cereal (wheat, gram), yeast, fish, meat, eggs, etc.	Affects central nervous system, causes weakness, convulsions, insomnia, anaemia
Vitamin B_{12}	Cyanocobalamin	Water	Egg, milk, liver of ox, sheep, fish, etc.	Pernicious anaemia
Vitamin C	Ascorbic acid	Water	Citrus fruits, chillies, sprouted, pulses, etc.	Pyorrhea, scurvy (bleeding of gums)
Vitamin D (a mixture of vitamins D_1 and D_3)	Ergocalciferol and cholecalciferol	Fat	Butter, milk, eggs, fish liver oil, liver and meat (Vitamin D_3 is produced in skin in presence of sunlight).	Rickets (bending of bones) and osteomalacia
Vitamin E	Tocopherol	Fat	Wheat gram oil, milk, nuts, peanut oil, cotton seed oil, egg, fish, etc.	Loss of fertility in males, muscle degeneration
Vitamin H	Biotin	–	Milk, yeast, liver, kidney, etc.	Dermatitis
Vitamin K	Phylloquinone	Fat	Leafy vegetables like cabbage, spinach, etc.	Haemorrhages and lengthens time of blood clotting

- The conditions of vitamin deficiency is known as *avitaminoses.*
- Water soluble vitamins cannot be stored in body and excess intake of fat soluble vitamins cause *hypervitaminoses.*

9. Which of the vitamins given below is water soluble?
    (a) Vitamin E   (b) Vitamin K
    (c) Vitamin C   (d) Vitamin D
                                    (JEE Main 2015)

Nucleic Acids
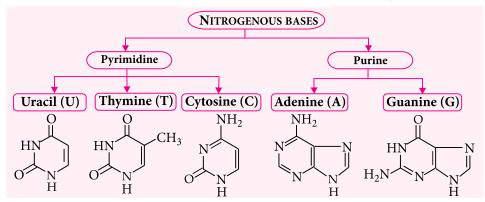
- Nucleic acids are polymers of nucleotides hence, they are called *polynucleotides.*

- They are present in nucleus of all living cells and are essential for heredity and biosynthesis of proteins.
- There are three basic components of each nucleotide monomeric unit. *viz*, pentose sugar, nitrogenous base and phosphate group.
  - *Pentose sugar :*

D-Ribose   D-2-Deoxyribose
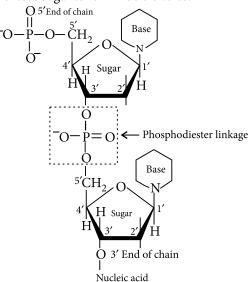
  - *Nitrogenous bases :* These are heterocyclic organic compunds having two or more nitrogen atoms in the ring.

- **Structure of nucleic acids :**
  - Nucleotides are joined together by phosphodiester linkages between 5′ and 3′ carbon atoms of pentose sugar to form nucleic acids.

- Two types of nucleic acids, *viz*, DNA and RNA are distinguished from each other in the following manner :

Deoxyribonucleic acid (DNA)	Components	Ribonucleic acid (RNA)
2-Deoxy-D-(–) ribose	**Sugar**	D-(–) Ribose
Cytosine and thymine	**Pyrimidine base**	Uracil and cytosine
Adenine and guanine	**Purine base**	Adenine and guanine
H_3PO_4	**Phosphoric acid**	H_3PO_4
Double stranded α-helix	**Structure**	Single stranded α-helix
Possible	**Replication**	Not possible

- **Chargaff's rule :** The rule describes base composition of a DNA molecule.
  - It states that amount of purine bases is always equal to that of pyrimidine bases.

- ○ Purine base of one strand of DNA molecule pairs with pyrimidine base of the other strand.
- ○ Adenine (A) pairs with thymine (T) through two H-bonds (A = T) and guanine (G) pairs with cytosine (C) through three H-bonds (G≡C).
- ○ In case of RNA, adenine (A) pairs with uracil (U), (A = U).

- ❑ **Biological functions of nucleic acids :**
  - ○ *Replication* : It is the enzyme catalysed process by which a single DNA molecule produces two identical copies of itself.
  - ○ *Protein synthesis* : It is carried out by RNA molecules in two steps.
    - – *Transcription* : It is the process of synthesis of RNA from DNA in the cytoplasm of the cell.
    - – *Translation* : The *m*-RNA directs the protein synthesis by this process.
  - ○ *Genetic code* : Linear sequences of three nucleotides (triplets) in DNA or RNA that determines the specific amino acid sequence in the synthesis of proteins is called genetic code. It is the biochemical basis of heredity and nearly universal in all organisms.
  - ○ *Mutation* : It is a change in nitrogenous base sequence of DNA molecule which leads to the synthesis of proteins with an altered sequence of amino acids. Mutation may cause genetic disorders or diseases.

🔑 **KEY** POINT

- • Sequence of three bases in *t*-RNA molecule is known as *anticodon* and useful during protein synthesis.
- • Separation of DNA strands on heating known as *melting* and hybridisation again on cooling is known as *annealing*.

✓ **SELF** CHECK

10. Which one of the following bases is not present in DNA?
 (a) Thymine (b) Quinoline
 (c) Adenine (d) Cytosine
 (JEE Main 2014)

11. The presence or absence of hydroxy group on which carbon atom of sugar differentiates RNA and DNA?
 (a) 1st (b) 2nd
 (c) 3rd (d) 4th (AIEEE 2011)
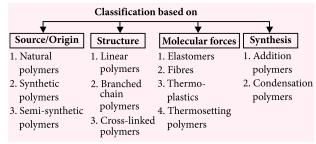
POLYMERS

- • Introduction
- • Classification
- • Methods of Polymerisation
- • Rubber
- • Some Important Polymers

TIPS TO REMEMBER

- ❑ A polymer is a naturally occurring or synthetic macromolecule made up of a linked series of a large number of repeated simple monomers.
- ❑ Polymers are formed by chemical reactions in which a large number of molecules called *monomers* are joined sequentially, forming a chain. This process is called *polymerisation*.

Classification of Polymers

Classification based on			
Source/Origin	**Structure**	**Molecular forces**	**Synthesis**
1. Natural polymers	1. Linear polymers	1. Elastomers	1. Addition polymers
2. Synthetic polymers	2. Branched chain polymers	2. Fibres	2. Condensation polymers
3. Semi-synthetic polymers	3. Cross-linked polymers	3. Thermo-plastics	
		4. Thermosetting polymers	

- ❑ **Natural polymers :** These are the substances of natural origin and are mainly found in plants and animals. *e.g.*, starch, cellulose, proteins, etc.
- ❑ **Synthetic polymers :** These are the polymers which are prepared in the laboratories, also called *man-made polymers*. *e.g.*, teflon, terylene, synthetic rubber, etc.
- ❑ **Semi-synthetic polymers :** They are mostly derived from naturally occurring polymers by chemical modifications. *e.g.*, vulcanised rubber, cellulose nitrate, etc.
- ❑ **Linear polymers :** These are the polymers in which monomers are linked together to form linear chains. *e.g.*, polyethene, polyester, nylon, etc.
- ❑ **Branched chain polymers :** These are the polymers in which the monomers are joined to form long chains or branches of different lengths. *e.g.*, glycogen, starch, etc.
- ❑ **Cross-linked polymers :** These are the polymers in which the monomer units are cross-linked together to form a three-dimensional network. They are also called *three-dimensional network polymers*. *e.g.*, bakelite, melamine, etc.

- **Elastomers :** These are the polymers having very weak intermolecular forces between the polymer chains. The weak forces permit the polymer to be stretched. Elastomers, thus possess elastic character. *e.g.*, vulcanised rubber.

- **Fibres :** They are the polymers which have strong intermolecular forces between the chains. These are either hydrogen bonds or dipole-dipole interactions. *e.g.*, nylon-6,6.

- **Thermoplastics :** They are the polymers in which the intermolecular forces of attraction are intermediate between those of elastomers and fibres. These polymers do not have any cross-links between the chains, they can be easily moulded on heating, *i.e.*, thermoplastics soften on heating and become hard on cooling. *e.g.*, polyethene, polystyrene, PVC, etc.

- **Thermosetting polymers :** They have extensive cross-links formed between polymer chains on heating. They undergo the permanent change on heating. *e.g.*, bakelite, melamine, etc.

- **Addition polymers :** They are formed by direct addition of repeated monomers without the elimination of by product molecules. The phenomenon is known as *addition polymerisation.*

- Addition polymers are of two types based on the number of types of monomers used.

  - *Homopolymer* : Polymer made up of only one type of monomer. *e.g.*, polythene.

    $$n\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{Polymerisation}} \left[\text{CH}_2 - \text{CH}_2\right]_n$$
    Ethene   Polythene

  - *Copolymer* : Polymer made up of two or more types of monomers. *e.g.*, buna-S. The process of formation of copolymer is called *copolymerisation.*

    - Copolymers have better physical and mechanical properties. The properties of copolymers could be changed by varying the amount of each monomer.

    $$n\text{CH}_2\text{=CH}-\text{CH=CH}_2 + n\text{CH}_2\text{=CH} \longrightarrow$$
    1,3-Butadiene $\underset{\text{CN}}{|}$
                                       Acrylonitrile

    $$\left[\text{CH}_2-\text{CH=CH}-\text{CH}_2-\text{CH}_2-\underset{\underset{\text{CN}}{|}}{\text{CH}}\right]_n$$
                            Buna-N

- **Condensation polymers :** They are formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, alcohol, etc. The phenomenon is known as *condensation polymerisation.*

$$n\text{HOCH}_2\text{CH}_2\text{OH} + n\text{CH}_3\text{OOC} - \langle\bigcirc\rangle - \text{COOCH}_3$$
Ethylene glycol   Dimethyl terephthalate

$$\xrightarrow[\text{C H}_3\text{OH}]{\Delta} \left[\text{CH}_2\text{CH}_2\text{OOC} - \langle\bigcirc\rangle - \text{COO}\right]_n$$
                             Terylene

Methods of Polymerisation

- **Addition (chain-growth) polymerisation :** This involves a number of steps, in each step a reactive particle is consumed and the similar one is produced. The monomers used are unsaturated compounds such as alkenes and their derivatives. Depending upon the reactive particles formed these are of three types, free radical, cationic and anionic.

  - *Mechanism of free radical polymerisation* : This is initiated by organic peroxides or by light. Steps involved are :

    - *Chain initiation :*
      $$\text{Peroxide} \xrightarrow{\text{heat}} \dot{R}(\text{Radical})$$

    - *Chain propagation :*
      $$\dot{R} + \text{CH}_2\text{=CH}_2 \longrightarrow R-\text{CH}_2-\dot{\text{C}}\text{H}_2$$
      $$R-\text{CH}_2-\dot{\text{C}}\text{H}_2+\text{CH}_2\text{=CH}_2 \longrightarrow$$
      $$R-\text{CH}_2-\text{CH}_2-\text{CH}_2-\dot{\text{C}}\text{H}_2$$
      $$R-\text{CH}_2-\text{CH}_2--\text{CH}_2-\dot{\text{C}}\text{H}_2 \longrightarrow \longrightarrow \longrightarrow$$
      $$R\left(\text{CH}_2-\text{CH}_2\right)_n\text{CH}_2-\dot{\text{C}}\text{H}_2$$

    - *Chain termination* :
      - *Combination* :
      $$2R\left(\text{CH}_2-\text{CH}_2\right)_n\text{CH}_2-\dot{\text{C}}\text{H}_2 \longrightarrow$$
      $$R\left(\text{CH}_2\text{CH}_2\right)_n\text{CH}_2\text{CH}_2-\text{CH}_2\text{CH}_2\left(\text{CH}_2\text{CH}_2\right)_n R$$

      - *Disproportionation* :
      $$2R\left(\text{CH}_2-\text{CH}_2\right)_n\text{CH}_2-\dot{\text{C}}\text{H}_2 \longrightarrow$$
      $$R\left(\text{CH}_2-\text{CH}_2\right)_n\text{CH=CH}_2$$
                         Alkene
      $$+$$
      $$R\left(\text{CH}_2-\text{CH}_2\right)_n\text{CH}_2-\text{CH}_3$$
                         Alkane

  e.g., polythene, polystyrene

- *Mechanism of cationic addition polymerisation :* Initiated by the use of strong Lewis acids such as HF, $AlCl_3$, H_2SO_4, etc.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

$$H^+ + CH_2 = CH_2 \longrightarrow CH_3 - CH_2^+$$

  - The so formed carbocation undergoes addition with several monomers and finally the chain is terminated by combination with a negative ion or loss of a proton. *e.g.*, polyvinyl ether, polyisobutylene, polystyrene, etc.

- *Mechanism of anionic addition polymerisation :* Initiated by strong bases such as $Na^+NH_2^-$, C_4H_9Li and Grignard reagent, etc.

$$B : + CH_2 = CH_2 \longrightarrow B - CH_2 - CH_2^-$$
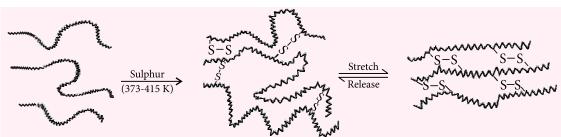$$\text{Carbanion}$$

  - The so formed carbanion undergoes addition with number of monomers and finally terminates. *e.g.*, polymerisation of acrylonitrile, vinyl chloride and methyl methacrylate, etc.

- ❑ **Condensation (step-growth) polymerisation :** These are formed by the condensation of two or more bifunctional monomer units with the elimination of simple molecules like H_2O, NH_3, CO_2, etc, *e.g.*, formation of nylon, terylene and bakelite, etc.

Rubber

- ❑ **Natural rubber :** It is a linear 1, 4-addition polymer of isoprene and have *cis*-configuration of all double bonds thus, known as *cis*-1, 4-polyisoprene.
  - It is insoluble in water, dilute acids and alkalies but soluble in organic solvents like benzene, petrol etc.
  - It has low elasticity and tensile strength.
  - It has weak intermolecular van der Waals forces.
  - Its natural *trans*-isomer is *gutta-percha* which is non-elastic.
- ❑ **Vulcanisation of rubber :** It is the process of heating natural rubber with sulphur at a temperature of 373-415 K.
  - Sulphur cross-links makes the rubber hard, tough with greater tensile strength.
  - Some additives like carbon black, zinc oxide etc are used to improve wearing properties.

Natural rubber, soft and sticky : No cross-links between the polymeric chains.

Vulcanised rubber: The hydrocarbon chains are held together by cross-linking chains of sulphur atoms.

When stretched, the chains are straighten out, but they cannot slip past each other because of polysulphide bridges. Thus, rubber can be stretched only to a limited extent. When the tension is removed, the chains tend to coil up again and the rubber resumes it original shape.

- ❑ **Synthetic rubber :** It is obtained by polymerising certain organic compounds which may have properties similar to rubber and some additional desirable properties. Most of these polymers are derived from butadiene derivatives. These are also vulcanised. For example, neoprene, styrene butadiene rubber (SBR), thiokol, silicones, polyurethane rubber.
  - *Neoprene rubber :* It is prepared by polymerisation of chloroprene. Neoprene is superior to natural rubber in its stability to aerial oxidation and its resistance to solvents.
  - *Styrene Butadiene Rubber (SBR) or Buna-S :* It is a polymer of buta-1,3-diene and styrene. It has less tensile strength than natural rubber.
  - *Nitrile rubber or Buna-N :* It is a polymer of buta-1,3-diene and acrylonitrile. It is resistant to the action of petrol, lubricating organic solvents, etc.

Some Important Polymers

Polymer	Structure of monomer	Structure of polymer	Uses
Polythene	$CH_2 = CH_2$	$\left[CH_2 - CH_2 \right]_n$	As insulator, packing material, household and laboratory ware.
Polystyrene	$\underset{\bigcirc}{CH} = CH_2$	$\left[\underset{\bigcirc}{CH} - CH_2 \right]_n$	As insulator, wrapping material, household articles and toys maker.
Polyvinyl chloride (PVC)	$CH_2 = CHCl$	$\left[CH_2 - \underset{Cl}{CH} \right]_n$	In manufacture of raincoats, hand bags, leather clothes and vinyl flooring.
Polytetrafluoro - ethylene (PTFE) or Teflon	$CF_2 = CF_2$	$\left[CF_2 - CF_2 \right]_n$	As lubricant, insulator and making cooking wares.
Polyacrylonitrile (PAN) or Orlon	$CH_2 = CH-CN$	$\left[CH_2 - \underset{CN}{CH} \right]_n$	In making synthetic fibres and wool.
Butyl rubber	$CH_2 = \underset{CH_3}{\overset{CH_3}{C}}$	$\left[CH_2 - \underset{CH_3}{\overset{CH_3}{C}} \right]_n$	Used in place of natural rubber in industry.
Neoprene	$CH_2 = \underset{Cl}{C} - CH = CH_2$	$\left[CH_2 - \underset{Cl}{C} = CH - CH_2 \right]_n$	As insulator, making conveyor belts and printing rollers.
Styrene Butadiene Rubber (SBR) or (Buna-S)	$\underset{\bigcirc}{CH} = CH_2$ and $CH_2 = CH - CH = CH_2$	$\left[CH_2 - \underset{\bigcirc}{CH} - CH_2 - CH = CH - CH_2 \right]_n$	In making automobile tyres, floor tiles, cable insulation and footwear.
Nitrile rubber (Buna-N)	$CH_2 = CHCN$ and $CH_2 = CH - CH = CH_2$	$\left[\underset{CN}{CH} - CH_2 - CH_2 - CH = CH - CH_2 \right]_n$	In making oil seals, hose-pipes and tank linings.
Nylon-6 (Perlon-L)	$\underset{N-H}{\bigcirc} = O$	$\left[\underset{O}{\overset{}{C}} - (CH_2)_5 - \underset{H}{N} \right]_n$	In making carpets, ropes and tyre cords.
Nylon-6, 6	$HOOC - (CH_2)_4 - COOH$ and $H_2N - (CH_2)_6 - NH_2$	$\left[CO - (CH_2)_4 - CONH - (CH_2)_6 - NH \right]_n$	Synthetic fibres, fishing nets, ropes and tyre industries.
Terylene (Dacron)	$CH_3OOC - \bigcirc - COOCH_3$ and $HOCH_2CH_2OH$	$\left[OOC - \bigcirc - COO - CH_2CH_2 \right]_n$	Synthetic fibres, safety belts, tyre cords and tents.
Bakelite (Phenol-formaldehyde resin	$\underset{\bigcirc}{OH}$ and $HCHO$	$\left[CH_2 - \underset{\bigcirc}{\overset{OH}{}} - CH_2 - \underset{\bigcirc}{\overset{OH}{}} - CH_2 \right]_n$	In making gears, protective coatings and electric fittings.

SELF CHECK

12. Which polymer is used in the manufacture of paints and lacquers?
    (a) Polypropene   (b) Polyvinyl chloride
    (c) Bakelite   (d) Glyptal
    <div align="right">(JEE Main 2015)</div>

13. Match the polymers in column-A with their main uses in column-B and choose the correct answer.

Column-A		Column-B	
(A)	Polystyrene	(i)	Paints and lacquers
(B)	Glyptal	(ii)	Rain coats
(C)	Polyvinyl chloride	(iii)	Manufacture of toys
(D)	Bakelite	(iv)	Computer discs

    (a) (A) - (ii), (B) - (i), (C) - (iii), (D) - (iv)
    (b) (A) - (iii), (B) - (i), (C) - (ii), (D) - (iv)
    (c) (A) - (ii), (B) - (iv), (C) - (iii), (D) - (i)
    (d) (A) - (iii), (B) - (iv), (C) - (ii), (D) - (i)
    <div align="right">(JEE Main 2015)</div>

14. Which one of the following structures represents the neoprene polymer?

    (a) $+CH_2-C=CH-CH_2\frac{}{}_n$
          $|$
          Cl

    (b) $+CH_2-CH\frac{}{}_n$
              $|$
              CN

    (c) $+CH_2-CH\frac{}{}_n$ (d) $+CH-CH_2\frac{}{}_n$
              $|$ $|$
              Cl C_6H_5
    <div align="right">(JEE Main 2015)</div>

15. Which one is classified as a condensation polymer?
    (a) Acrylonitrile   (b) Dacron
    (c) Neoprene   (d) Teflon
    <div align="right">(JEE Main 2014)</div>

16. The species which can best serve as an initiator for the cationic polymerisation is

    (a) HNO$_3$ (b) AlCl$_3$
    (c) BuLi   (d) LiAlH$_4$ (AIEEE 2012)

17. The polymer containing strong intermolecular forces *e.g.*, hydrogen bonding is
    (a) natural rubber   (b) teflon
    (c) nylon-6,6   (d) polystyrene.
    <div align="right">(AIEEE 2010)</div>

CHEMISTRY IN EVERYDAY LIFE

- Chemicals in Medicines
- Chemicals in Food
- Cleansing Agents

TIPS TO REMEMBER

Chemicals in Medicines (drugs)

- In a general way, the drug may be defined as a substance used in the prevention, diagnosis, treatment or cure of disease in man or other animals.

- **Antacids :** Drugs which neutralise acidity or raise the pH of stomach to some appropriate level. Baking soda, metal hydroxides like $Al(OH)_3$, $Mg(OH)_2$, cimetidine, ranitidine, lansoprazole, omeprazole are few examples of antacids.

- **Antihistamines (anti-allergic drugs) :** Drugs which interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.

  ○ Histamines are the chemicals released by mast cells during an allergic reaction.

  ○ Diphenylhydramine (Benadryl), pheniramine maleate (avil), chlorpheniramine (zeet) are few examples of antihistamines.

- **Neurologically active drugs :** Tranquilizers and analgesics are neurologically active drugs. These affect the message transfer mechanism from nerve to receptor.

- **Tranquilizer :** It is a class of chemical compounds used for the treatment of stress, mild and severe mental diseases. These are commonly called *psychotherapeutic drugs*. These are the essential component of sleeping pills. Some examples according to the action of drugs are :

  ○ *Narcotics* : They reduce anxiety and tension. *e.g.*, heroin, pethidine, etc.

THE *p*-BLOCK ELEMENTS (Group 13)

B
Al
Ga
In
Tl

Group 13 is the first group to span the dividing line between metals and non-metals and its chemistry is more diverse than that of groups 1 and 2.

Atomic and Physical Properties

- **Elements :** B, Al, Ga, In, Tl
- **Electronic configuration :** [Noble gas]ns^2np^1
- **Oxidation States :** +1 and +3
- **Metallic Character :** $\underset{\text{Metalloid}}{B,}$ $\underset{\text{Metals}}{Al, Ga, In, Tl}$
- **Atomic radii, ionic radii, density and stability of +1 oxidation state :** Generally increase down the group however, the atomic radius of Ga is lower than that of Al.
- **Boiling points and stability of +3 oxidation state :** Decrease down the group.
- **Electronegativity :** First decreases from B to Al then increases from Al to Ga and then decreases marginally down the group.
- **Melting points :** Decrease from B to Ga and then increase.
- **Ionisation energy :** B > Tl > Ga > Al > In
- **Lewis acids :** BCl_3, $AlCl_3$ etc. behave as Lewis acids due to incomplete octet.
- **Complex formation :** Due to small size, high charge density and availability of vacant *d*-orbitals.

Chemical Properties

- **Reactivity towards air :**
  - $4E + 3O_2 \xrightarrow{\Delta} 2E_2O_3$ (E = Group 13 elements)
  - $\underset{\text{Acidic}}{B_2O_3}$, $\underset{\text{Amphoteric}}{Al_2O_3 \quad Ga_2O_3}$ $\underset{\text{Basic}}{In_2O_3 \quad Tl_2O}$
  - $2E + N_2 \xrightarrow{\Delta} 2EN$ (Except Ga, In, Tl)
- **Reactivity towards acids :**
  - B reacts only with strong oxidising acids at high temperature.
  - $B + 3HNO_3 \xrightarrow[\Delta]{\text{conc. } H_2SO_4} H_3BO_3 + 3NO_2$
  - All other elements react with both, non-oxidising and oxidising acids liberating H_2 gas.
  - Al becomes passive with conc. HNO_3 due to the formation of a thin protective layer of its oxide (Al_2O_3) on the surface of the metal which prevents it from further action.
- **Reactivity towards alkalies :**
  - $2B + 6KOH \xrightarrow{> 773 \text{ K}} 2K_3BO_3 + 3H_2$
  - $2E + 2NaOH + 6H_2O \longrightarrow 2Na^+[E(OH)_4]^- + 3H_2$ (E = Al, Ga)
- **Reactivity towards halogens :**
  - $2E + 3X_2 \longrightarrow 2EX_3$ (Except TlI_3)
    (X = F, Cl, Br, I)

GROUP 13 : THE BORON FAMILY

Anomalous Behaviour of Boron

- Difference in behaviour of B is due to small size, high ionisation energy and absence of *d*-orbitals.
- B is extremely hard having high m.pt and b.pt.
- B shows maximum covalency of 4 while rest of the elements show maximum covalency of 6.
- B exhibits allotropy.
- B forms only covalent compounds.

Important Compounds of Boron

Diborane (B_2H_6)

- **Preparation :**
  - *Laboratory method :*
  - $2NaBH_4 + I_2 \xrightarrow{\text{Diglyme}} B_2H_6 + 2NaI + H_2$
  - *Industrial method :*
  - $2BF_3 + 6NaH \xrightarrow{450 \text{ K}} B_2H_6 + 6NaF$
- **Properties :**
  - Colourless, highly toxic gas.
  - $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$
  - $B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2$
  - $3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} \underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$
- **Structure :**
  - *Four bonds :* 2 centre-2 electron type
  - *Two bonds :* 3 centre-2 electron type (*banana bonds*)

Orthoboric acid (H_3BO_3)
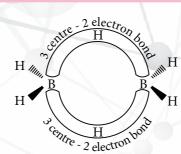
- **Preparation :**
  - $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$
- **Properties :**
  - White crystalline solid with a soapy touch.
  - Planar BO_3^{3-} units joined by H-bonds to form layer structure of boric acid.
  - *Monobasic acid :*
  - $B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$
  - $H_3BO_3 \xrightarrow{370 \text{ K}} \underset{\substack{\text{Metaboric} \\ \text{acid}}}{HBO_2} + H_2O$
  - $4HBO_2 \xrightarrow[-H_2O]{410 \text{ K}} \underset{\substack{\text{Tetraboric} \\ \text{acid}}}{H_2B_4O_7} \xrightarrow[\text{heat}]{\text{Red}} \underset{\substack{\text{Boron} \\ \text{trioxide}}}{2B_2O_3} + H_2O$
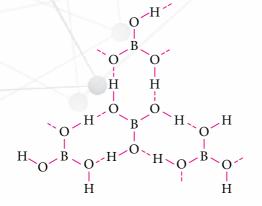
Borax ($Na_2[B_4O_5(OH)_4].8H_2O$)

- **Preparation :**
  - $Ca_2B_6O_{11} + 2Na_2CO_3 \xrightarrow{\Delta} Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3$
  - $4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$
- **Properties :**
  - White crystalline solid.
  - $Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + 4H_3BO_3$
  - $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\substack{\text{Sodium} \\ \text{metaborate}}}{2NaBO_2} + \underset{\text{Borax bead}}{B_2O_3}$

- *Sedatives* : They reduce the action of central nervous system. *e.g.*, valium, barbiturates.
- *Antidepressants* (*mood boosters*) : They reduce depression, *e.g.*, iproniazid, phenelzine, etc.
- Chlordiazepoxide and meprobamate are relatively mild tranquilizers suitable for relieving tension. Equanil is used in controlling depression and hypertension.
- *Hypnotics* (*sleep producing drugs*): Barbiturates such as seconal, luminal, veronal.
- *Non-hypnotic drugs :* Valium and serotonin.

- **Analgesics :** Drugs which relieve pain without causing impairment of consciousness, mental confusion, paralysis.
  - *Non-narcotics* : Drugs which do not cause addiction. *e.g.*, aspirin, paracetamol are analgesics as well as antipyretics. Aspirin is also used in prevention of heart attack due to its anticlotting property.
  - *Narcotics* : Their chronic use leads to addiction. *e.g.*, morphine, codeine, etc.

- **Antimicrobials :** Antimicrobials tend to prevent development or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (anti fungal agents), virus (antiviral agents) or other parasites (anti parasitic drugs) selectively.

- **Antibiotics :** These are the chemicals synthesised from microbes and have either cidal (killing) effect or a static (inhibitory) effect on microbes.
  - Depending upon the range of microorganisms affected; antibiotics are classified as broad spectrum antibiotics and narrow spectrum antibiotics.
    - Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be *broad spectrum antibiotics*. *e.g.,* ampicillin, amoxycillin, ofloxacin etc.
    - Antibiotics which are effective mainly against Gram-positive or Gram-negative bacteria are *narrow spectrum antibiotics e.g.*, pencillin

- **Antiseptics :** These are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces. *e.g.*, furacine, soframicine, dettol (a mixture of chloroxylenol and terpineol), 0.2% solution of phenol.
- **Disinfectants :** These substances kill or stop the growth of microorganisms but are harmful to living cells hence they are used on non-living objects like clothes, floors, utensils, etc. For example phenol, bleaching powder, H_2O_2, etc.
- **Antifertility drugs :** These drugs are used to reduce birth rates *e.g.*, mifepristone, silphium, etc.

Chemicals in Food

- Chemicals which are added to food for their preservation or enhancing their appeal, flavour, etc. are known as *food additives*.
- **Food preservatives :** These are the chemical substances which are added to the food materials to prevent their spoilage and to retain their nutritive value for long periods.
  - These preservatives prevent the rancidity of food and inhibit the growth or kill the microorganisms.
  - The most common preservative used is sodium benzoate (C_6H_5COONa).
- Certain food preservatives such as BHA and BHT used for edible oils also act as antioxidants.
- **Artificial sweetening agents :** These are chemical compounds which give sweetening effect to the food and enhance its odour and flavour.

Artificial sweetener	Sweetness value in comparison to cane sugar
Aspartame	100
Sccharin	550
Sucralose	600
Alitame	2000

- **Antioxidants :** These are the chemical substances which prevent oxidation and subsequent spoilage of the food by retarding the action of oxygen on food. They act as sacrificial materials as they are more reactive towards oxygen than the materials they are protecting. They also reduce the rate of involvement of free radicals in the ageing process.

Cleansing Agents

- **Soaps :** These are sodium or potassium salts of higher fatty acids (with 12-18 carbon atoms). *e.g.*, salts of $C_{15}H_{31}COOH$ (palmitic acid), $C_{17}H_{35}COOH$ (stearic acid), $C_{17}H_{33}COOH$ (oleic acid), $C_{17}H_{31}COOH$ (linoleic acid), etc.

- **Soapless soaps or synthetic detergents :** These are sodium salts of long chain alkyl hydrogen sulphates or the sodium salts of long chain benzene sulphonic acids.

  - *Cationic detergents :* These are quaternary ammonium salts of amines with acetates or halides as anions. *e.g.*, trimethylstearylammonium chloride, $CH_3(CH_2)_{17}\overset{+}{N}(CH_3)_3Cl^-$

  - *Anionic detergents :* These contain anionic hydrophilic groups *e.g.*, sodium lauryl sulphate, $C_{12}H_{25}OSO_3^-Na^+$
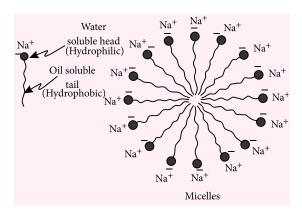
  - *Non-ionic detergents :* These are esters of high molecular mass and do not contain ions. *e.g.,* polyethyleneglycol stearate, $CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$

- **Advantages of synthetic detergents over soaps :**

  - They can be used in hard water, in acidic medium while soaps get precipitated.

  - They are more soluble in water and thus, form lather more easily.

  - They are stronger cleansing agents than soaps as they decrease the surface tension to greater extent.

- **Cleansing action of soaps and detergents :**

  - The hydrophilic carboxylate group interact with water molecules while the hydrophobic long non-polar hydrocarbon chain does not interact.

  - The hydrocarbon chains cluster together forming structure called micelles.

  - In the micelles, the carboxylate groups form a negatively-charged spherical surface, with the hydrocarbon chains inside the sphere.

  - Being negatively charged, soap micelles repel each other and remain dispersed in water.

Micelles

✓ SELF CHECK

18. Which of the following compounds is not an antacid?
    - (a) Phenelzine
    - (b) Ranitidine
    - (c) Aluminium hydroxide
    - (d) Cimetidine   (JEE Main 2015)

19. [structure: benzene ring with OCOCH₃ and COOH] is used as
    - (a) insecticide   (b) antihistamine
    - (c) analgesic   (d) antacid.

                            (JEE Main 2015)

20. Which artificial sweetener contains chlorine?
    - (a) Aspartame   (b) Saccharin
    - (c) Sucralose   (d) Alitame

                            (JEE Main2015)

21. Aspirin in known as
    - (a) phenyl salicylate
    - (b) acetyl salicylate
    - (c) methyl salicylic acid
    - (d) acetyl salicylic acid   (JEE Main 2012)

ANSWER KEYS (SELF CHECK)									
1.	(a)	**2.**	(c)	**3.**	(b)	**4.**	(c)	**5.**	(c)
6.	(a)	**7.**	(a)	**8.**	(b)	**9.**	(c)	**10.**	(b)
11.	(b)	**12.**	(d)	**13.**	(b)	**14.**	(a)	**15.**	(b)
16.	(b)	**17.**	(c)	**18.**	(a)	**19.**	(c)	**20.**	(c)
21.	(d)								

❑❑❑

Exam Café

1. (+)-Glucose and (–)-fructose can be differentiated by
   (a) Tollens' reagent   (b) Benedict's solution
   (c) bromine water   (d) none of these.

2. Which of the following statements is not true?
   (a) Some disinfectants can be used as antiseptics at low concentration.
   (b) Sulphadiazine is a synthetic antibacterial.
   (c) Ampicillin is a natural antibiotic.
   (d) Aspirin is both, an analgesic and an antipyretic.

3. Formation of polyethylene from calcium carbide takes place as follows :
   $$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$
   $$C_2H_2 + H_2 \longrightarrow C_2H_4$$
   $$nC_2H_4 \longrightarrow (—CH_2 — CH_2 —)_n$$
   The amount of polyethylene obtained from 64 kg of CaC_2 is
   (a) 7 kg   (b) 14 kg
   (c) 21 kg   (d) 28 kg

4. The primary structure of a protein refers to
   (a) whether the protein is fibrous or globular
   (b) the amino acid sequence in the polypeptide
   (c) the orientation of the amino acid side chains in space
   (d) the presence or absence of an α-helix.

5. Which of the following is used for inducing sleep?
   (a) Paracetamol   (b) Chloroquine
   (c) Bithional   (d) Barbituric acid derivatives

6. Which of the following can be remelted again and again without producing any change?
   (a) Urea formaldehyde resin
   (b) PVC
   (c) Bakelite
   (d) Melamine formaldehyde resin

7. During the process of digestion, the proteins present in food material are hydrolysed to amino acids in the following two stages :

   Protein $\xrightarrow{\text{Enzyme } A}$ Polypeptides $\xrightarrow{\text{Enzyme } B}$ Amino acids

   A and B are respectively

   (a) pepsin and trypsin
   (b) invertase and zymase
   (c) amylase and maltase
   (d) diastase and lipase.

8. The structure given below represents

   (a) Penicillin-F   (b) Penicillin-G
   (c) Penicillin-K   (d) Ampicillin

9. Which of the following is not correctly matched?

   (a) Neoprene :

   (b) Nylon-6,6 :

   (c) Terylene :

   (d) PMMA :

10. Mark the wrong statement about enzymes.
    (a) Enzymes are biological catalysts.
    (b) Each enzyme can catalyse a number of similar reactions.
    (c) Enzymes are very efficient catalysts.
    (d) Enzymes are needed only in very small amounts for their action.

11. Which of the following is biodegradable?

(a) $C_{17}H_{35}COONa$

(b) $CH_3-\left[CH-CH_2\right]_3-CH-\langle O \rangle-SO_3Na$
       with CH_3 and CH_3 substituents

(c) $CH_3-(CH_2)_{11}-\langle O \rangle-SO_3Na$

(d) Both (a) and (c)

12. The monomer of the given polymer

$$\text{wwwCH}_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-C\overset{CH_3}{\underset{CH_3}{}}\text{www}$$

(a) $H_2C=C\overset{CH_3}{\underset{CH_3}{}}$

(b) $(CH_3)_2C=C(CH_3)_2$

(c) $CH_3-CH=CH-CH_3$

(d) $CH_3-CH=CH_2$

13. An organic compound with the formula $C_6H_{12}O_6$, forms a yellow crystalline solid with phenylhydrazine and gives a mixture of sorbitol and mannitol when reduced with sodium. Which among the following could be the compound?

(a) Fructose   (b) Glucose
(c) Mannose   (d) Sucrose

14. Antiseptics and disinfectants either kill or prevent growth of micro-organisms. Identify which of the following statements is not true?

(a) Dilute solution of boric acid and hydrogen peroxide are strong antiseptics.
(b) Disinfectants harm the tissues.
(c) A 0.2% solution of phenol is an antiseptic while 1.0% solution is disinfectant.
(d) Tincture of iodine is a powerful antiseptic.

15. Which of the following fibres is not an addition copolymer?

(a) Saran   (b) Buna-N
(c) SBR   (d) Nylon-6, 10

16. The mutarotation of glucose is characterised by

(a) a change from an aldehyde to ketone structure
(b) a change of specific rotation from a (+) to a (−) value
(c) the presence of an intramolecular bridge structure

(d) the irreversible change from α-D to the β-D form.

17. The drug given during hypertension is

(a) streptomycin   (b) savlon
(c) equanil   (d) aspirin.

18. Which one of the following statements is not true?

(a) Buna-S is a copolymer of butadiene and styrene.
(b) Natural rubber is a 1, 4-polymer of isoprene.
(c) In vulcanisation, the formation of sulphur bridges between different chains make rubber harder and stronger.
(d) Natural rubber has the *trans*-configuration at every double bond.

19. An electric current is passed through an aqueous solution (buffered at pH = 6.0) of alanine (pI = 6.0) and ariginine (pI = 10.2). The two amino acids can be separated because

(a) alanine migrates to anode, and arginine to cathode
(b) alanine migrates to cathode and arginine to anode
(c) alanine does not migrate while arginine migrates to cathode
(d) alanine does not migrate while arginine migrates to anode.

20. A drug that is antipyretic as well as analgesic is

(a) chloropromazine hydrochloride
(b) *para*-Acetamidophenol
(c) chloroquine
(d) penicillin.

21. Which of the following is a biodegradable polymer?

(a) $+CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2+_n$

(b) $+CH_2-CH=CH-CH_2-CH_2-\underset{\underset{CN}{|}}{CH}+_n$

(c) $+O-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{||}}{C}-O-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{||}}{C}+_n$

(d) $+\underset{\underset{H}{|}}{N}-(CH_2)_6-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{||}}{C}-(CH_2)_4-\overset{\overset{O}{||}}{C}+_n$

22. Which statement is incorrect about peptide bond?

(a) C—N bond length in proteins is almost same as usual C—N bond length.

(b) Spectroscopic analysis shows planar structure of —C—NH— bond.
$$\underset{O}{\overset{\|}{C}}$$

(c) C—N bond length in proteins is smaller than usual C—N bond length.

(d) None of these.

23. Drug action if based on switching on the receptor by imitating the natural chemical is called
(a) agonist   (b) antagonist
(c) receptor   (d) none of these.

24. Polymerisation does not occur through intermediate formation of
(a) carbocations   (b) carbanions
(c) free radicals   (d) carbenes.

25. If the sequence of bases in one strand of DNA is ATGACTGTC then, the sequence of bases in its complementary strand is
(a) TACTGACAG   (b) TUCTUGUCCUG
(c) GUAGTUAUG   (d) None of these.

26. The sweetest artificial sugar among the following is
(a) aspartame   (b) sucralose
(c) alitame   (d) sucrose.

27. Which of the following is a biopolymer ?
(a) Nylon   (b) Leather
(c) Bakelite   (d) Orlon

28. An organic compound consumes 4 moles of periodic acid to form following compounds per mole of the starting compound HCHO, 3HCOOH and CHOCOOH. The organic compound is
(a) glucose   (b) fructose
(c) gluconic acid   (d) sorbitol.

29. Substance used for the preservation of jams, squashes etc. is
(a) benzene   (b) sodium metabisulphite.
(c) phenol   (d) none of these.

30. Match List-I (Monomer) with List-II (Polymer) and select the correct answer using the codes given below the lists :

List-I	List-II
I. Hexamethylenediamine	A. Bakelite
II. Phenol	B. Dacron
III. Phthalic acid	C. Glyptal
IV. Terephthalic acid	D. Polystyrene
	E. Nylon

Codes :
(a) I-E, II-A, III-B, IV-C
(b) I-E, II-A, III-C, IV-B
(c) I-D, II-C, III-A, IV-B
(d) I-D, II-C, III-A, IV-E

SOLUTIONS

1. **(c) :** Bromine water, a mild oxidising agent, oxidises only glucose (aldoses, in general) to gluconic acid. Tollens' reagent and Benedict's solution being alkaline in nature, cause isomerisation of fructose to glucose hence, both of them react with these reagents.

2. **(c) :** Ampicillin is a synthetic modification of penicillin.

3. **(d) :** The concerned chemical reactions are
(i) $\underset{64\ kg}{CaC_2} + 2H_2O \longrightarrow Ca(OH)_2 + \underset{Ethyne,\ 26\ kg}{C_2H_2}$

(ii) $C_2H_2 + H_2 \longrightarrow \underset{Ethylene,\ 28\ kg}{C_2H_4}$

(iii) $\underset{\substack{n \times 28\ kg \\ or\ 28\ kg}}{nC_2H_4} \longrightarrow \underset{\substack{n \times 28\ kg\ polythene \\ or\ 28\ kg}}{[-CH_2-CH_2-]_n}$

Thus, 64 kg of CaC_2 gives 26 kg of acetylene which in turn gives 28 kg of ethylene whose 28 kg gives 28 kg of the polymer, polythene.

4. **(b)**

5. **(d)**

6. **(b) :** Bakelite, urea formaldehyde resin and melamine formaldehyde resin are thermosetting polymers while PVC is a thermoplastic and can be used time and again.

7. **(a)**

8. **(b)**

9. **(b) :** Nylon-6,6 is a polyamide hence, it has only —CONH— linkage and no —COO— linkage.

10. **(b) :** Enzymes are highly specific catalysts. Each enzyme can catalyse only one chemical reaction.

11. **(d) :** Soaps are 100% biodegradable and high degree of branching in a detergent makes it non-biodegradable.

12. **(a) :** $CH_2{=}C\underset{CH_3}{\overset{CH_3}{\diagdown}}$ opens up as $-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-$ repeating unit.

13. **(a) :** Since the compound forms a yellow crystalline solid *i.e.*, osazone with phenylhydrazine, it may be an aldohexose or a ketohexose. Further, since on reduction, compound forms a mixture of sorbitol and mannitol, it must be a ketohexose, *i.e.*, fructose. Glucose on reduction gives only sorbitol.

14. **(a)**

15. **(d):** Nylon-6,10 is a condensation polymer formed from $NH_2(CH_2)_6NH_2$ and $HOOC(CH_2)_8COOH$.

16. **(c)**

17. **(c)**

18. **(d):** Natural rubber has *cis*-configuration at every double bond. The *trans*-isomer is gutta percha.

19. **(c) :** At the given pH (6) of the solution, alanine (pI = 6.0), exists as a dipolar ion while arginine (pI = 10.2) exists as a cation. Hence, on passing an electric current, alanine will not migrate to any electrode while arginine will migrate to cathode.

20. **(b)**

21. **(c) :** It is poly – β –hydroxybutyrate —co — β –hydroxy valerate (PHBV) which is biodegradable. All others are non-biodegradable polymers.

22. **(a) :** Due to resonance,

$$-\overset{\overset{O}{\|}}{C}-\ddot{N}H- \longleftrightarrow -\overset{\overset{O^-}{|}}{C}=\overset{+}{N}H-,$$

C—N bond acquires some double bond character, hence, it is shorter in length.

23. **(a)**

24. **(d) :** Carbenes are not formed during polymerisation.

25. **(a) :** In DNA, guanine (G) pairs with cytosine (C) and adenine (A) with thymine (T). If one strand of DNA has the sequence of bases as ATGACTGTC, the sequence of its complementary strand is TACTGACAG.

26. **(c) :** Aspartame is 100 times as sweet as sucrose
Sucralose is 600 times as sweet as sucrose.
Alitame is 2000 times as sweet as sucrose.

27. **(b):** Leather is an animal protein.

28. **(c) :**

$$\underset{\overset{|}{OH}}{CH_2}-\underset{\overset{|}{OH}}{CH}-\underset{\overset{|}{OH}}{CH}-\underset{\overset{|}{OH}}{CH}-\underset{\overset{|}{OH}}{CH}-COOH \xrightarrow{4HIO_4}$$

$$HCHO + 3HCOOH + H\underset{\overset{\|}{O}}{C}COOH$$

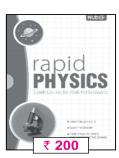29. **(b):** Preservative action of sodium metabisulphite is due to SO_2 which dissolves in water to give sulphurous acid.
$Na_2S_2O_5 \rightarrow Na_2SO_3 + SO_2$
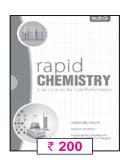$SO_2 + H_2O \rightarrow H_2SO_3$
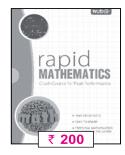Sulphurous acid inhibits the growth of yeasts, bacteria etc.

30. **(b)**

❑❑❑

ACE

YOUR WAY CBSE XII

PRACTICE PAPER 2016
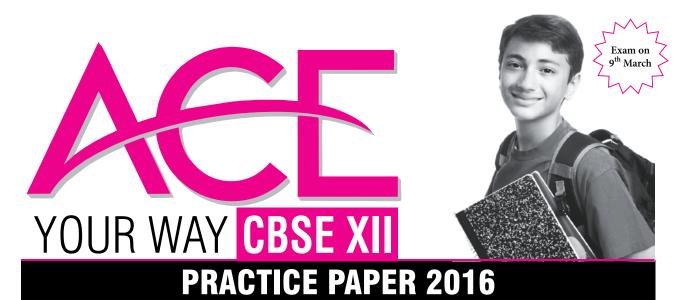
Time Allowed : 3 hours   Maximum Marks : 70

GENERAL INSTRUCTIONS

(i)   All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v)   Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. An organic compound C_8H_{18} on chlorination gives a single monochloride. Write the structure of the hydrocarbon.

2. Pure silicon is an insulator then, how does it behave as a semiconductor on heating?

3. Explain why the bond angle (C—O—C) in ether is slightly greater than the tetrahedral angle (109.5°28')?

4. Which of the following electrolyte is most effective for the coagulation of $Fe(OH)_3$ sol and why?
Na_3PO_4, Na_2SO_4, NaCl

5. Comment on how sulphuric acid is a dibasic acid.

6. The partial pressure of ethane over a saturated solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what would be the partial pressure of the gas?

7. How will you bring about the following conversions?
   (i) Propanone to propene
   (ii) Benzoic acid to *m*-nitrobenzyl alcohol

8. Explain the following observations :
   (i) Many of the transition elements are known to form interstitial compounds.
   (ii) There is a general increase in density from titanium ($Z = 22$) to copper ($Z = 29$).

9. For the cell $Zn|Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)}|Cu$, derive the relation between E°_{cell} and K_c at 298 K.

10. Write the formulae of the following complexes :
    (i)   Triamminetriaquachromium(III) chloride
    (ii) *Tris*(ethane-1, 2-diammine)cobalt(III) sulphate
    (iii) Diamminesilver(I) dicyanoargentate(I)
    (iv) Mercury(I)tetrathiocyanatocobaltate(III)

    OR

    The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion.

11. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallises in cubic lattice. If the density is 2 g/cc, then find the radius (in pm) of metal atom. (Given, $N_A = 6 \times 10^{23}$).

12. Write the chemical equations for synthesis of following polymers :
    (i)   Teflon   (ii) PVC
    (iii) Glyptal

13. (i) What is meant by van't Hoff factor?
    (ii) The osmotic pressure of a 0.0103 molar solution of an electrolyte is found to be 0.70 atm at 27°C. Calculate the van't Hoff factor.
    ($R = 0.082$ L atm mol^{-1} K^{-1}).
    What conclusion do you draw about the molecular state of the solute in the solution?

14. How can reducing and non-reducing sugars be distinguished? Mention the structural feature characterising reducing sugars.

15. Calculate the standard cell potential of the given galvanic cell in which the following reaction takes place :
$$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Cd_{(s)}$$
Given : $E^{\circ}_{Cr^{3+}/Cr} = -0.74$ V, $E^{\circ}_{Cd^{2+}/Cd} = -0.40$ V
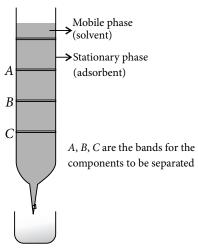Also, calculate $\Delta_r G^{\circ}$ and equilibrium constant of the reaction.

OR

Calculate the standard cell potential, $\Delta_r G^{\circ}$ and equilibrium constant for the reaction :
$$Fe^{2+}_{(aq)} + Ag^{+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Ag_{(s)}$$
Given : $E^{\circ}_{Fe^{3+}/Fe^{2+}} = -0.77$ V, $E^{\circ}_{Ag^{+}/Ag} = 0.80$ V

16. Give explanation for the following statements :
    (i) Chloroacetic acid has lower pK_a value than acetic acid.
    (ii) Carboxylic acids have higher boiling points than alcohols of comparable molecular masses.
    (iii) Sodium bisulphite is used for the purification of aldehydes and ketones.

17. Explain what happens when
    (i) ethanol vapours are passed over alumina at 600 K.
    (ii) excess of ethanol is heated with conc. H_2SO_4 at 413 K.
    (iii) phenol is treated with acetyl chloride.

18. Explain the following phenomenon giving reasons :
    (i) Rate of physical adsorption decreases with rise of temperature.
    (ii) Brownian movement
    (iii) Colloidal particles scatter light.

19. Give reasons for the following statements :
    (i) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.
    (ii) (±) 2-Butanol is optically inactive.
    (iii) C—X bond length in halobenzene is smaller than C—X bond length in CH_3—X.

20. Consider the following chromatogram of column chromatography :

Answer the following questions :
    (i) Which substance can act as stationary phase?
    (ii) Which of the three components A, B and C is eluted first of all?
    (iii) What is the principle of this technique?

21. Write short notes on :
    (i) Ionisation isomerism
    (ii) Linkage isomerism
    (iii) Coordination isomerism.

22. Account for the following statements :
    (i) Cerium (atomic number = 58) forms tetrapositive ion, Ce^{4+} in aqueous solution.
    (ii) The second and third members in each group of transition element have similar atomic radii.
    (iii) Write the structures of
    (a) MnO_4^- (b) CrO_5

23. A local resident, Shyam observed that some people wash clothes in the Ganga river everyday and some people wash their cars, scooters, rickshaw etc. too. At the same time, local residents consumed the same water. Shyam held a resident's meeting to educate people to stop polluting the river water. During the meeting a local resident, Vidhu resisted this by arguing that running water of river which is in huge amount does not get polluted by washing clothes and vehicles.
    (i) How does river water get polluted by washing clothes and vehicles using detergents?
    (ii) What values are displayed by Shyam?
    (iii) How many categories of detergents are there?

24. (i) The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is a first order reaction.

    (a) After 50 seconds at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

    (b) Calculate the pressure of Cl_2O_7 after 100 sec of decomposition at this temperature.

(ii) One-fourth of a first order reaction is completed in 32 minutes. What is the half-life period of this reaction?

<div align="center">OR</div>

Explain the following statements :

(i) Average rate of reaction does not give the true picture of the reaction rate.

(ii) A lump of coal burns at a moderate rate in air while coal dust burns explosively.

(iii) It takes more time to boil an egg or cook rice at higher altitudes.

(iv) Hydrogen and oxygen do not react at room temperature.

(v) How is rate constant related to concentration of the reactants?

25. (i) Arrange the following in decreasing order of property indicated :

    (a) H_2O, H_2S, H_2Se, H_2Te (Boiling point)

    (b) NH_3, PH_3, AsH_3, SbH_3 (Base strength)

(ii) Account for the following observations :

    (a) The +5 oxidation state of phosphorus is stable but not for bismuth.

    (b) Nitrogen forms a number of oxides while fewer number of oxides are possible for other elements of the group.

    (c) Hydrogen fluoride has higher boiling point than hydrogen chloride.

<div align="center">OR</div>

(i) Account for the following statements :

    (a) Decomposition of O_3 molecule is a spontaneous process.

    (b) SF_6 is inert towards hydrolysis.

    (c) H_2S is less acidic than H_2Te.

    (d) SO_2 is an air pollutant.

(ii) What happens when white phosphorus is heated with conc. NaOH solution in an inert gas atmosphere?

26. (i) An organic compound *(A)* with molecular formula $C_9H_{13}N$ dissolves in dil. HCl and releases N_2 with nitrous acid giving an optically active alcohol *(B)*. The alcohol *(B)* on oxidation gives dicarboxylic acid which on heating forms an anhydride. Identify the compounds *(A)* and *(B)*.

(ii) Give plausible explanations for the following :

    (a) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.

    (b) Tertiary amines do not undergo acylation reaction.

<div align="center">OR</div>

(i) An aromatic compound, C_7H_8 *(A)* on nitration gives *(B)* as a major product which on reduction with Sn/HCl gives *(C)*. The compound *(C)* on treatment with $NaNO_2$/HCl at 273 K following by subsequent treatment with CuCl/HCl gives *(D)*. When *(D)* is oxidised, it forms *ortho*-substituted monocarboxylic acid with the formula $C_7H_5O_2Cl$. Predict the structures of *(A)*, *(B)*, *(C)* and *(D)*.

(ii) Outline the steps for the conversion of methylcyanide to methylamine.

<div align="center" style="background-color:#e5007e;color:white;">SOLUTIONS</div>

1. As C_8H_{18} on chlorination gives a single mono-chloride therefore, all the hydrogen atoms in it are equivalent. The possible structure of the hydrocarbon is

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

2. On heating some covalent bonds among silicon atoms break and electrons become free to move under applied field hence, silicon behaves like a semiconductor at high temperature.

3. There are two lone pairs on oxygen which cause lone pair-bond pair repulsions and hence, bond angle (C—O—C) should decrease and have value less than 109°28' but steric hindrance of bulky alkyl groups causes increase in bond angle from 109.5°28' to 111.7°.

4. $Fe(OH)_3$ is a positively charged sol hence, the anion having maximum charge will be more effective in coagulation. Therefore, Na_3PO_4 having PO_4^{3-} ion (charge = –3) will be most effective.

5. H_2SO_4 forms two series of salts, *i.e.*, both the hydrogen atoms are replaceable.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$$

$$H_2SO_4 + NaOH \rightarrow \underset{\substack{\text{Sodium hydrogen} \\ \text{sulphate (Acid salt)}}}{NaHSO_4} + H_2O$$

$$H_2SO_4 + 2NaOH \rightarrow \underset{\substack{\text{Sodium sulphate} \\ \text{(Normal salt)}}}{Na_2SO_4} + 2H_2O$$

6. According to Henry's law, $m = K_H \times p$
Case I: 6.56×10^{-3} g $= K_H \times 1$ bar
or, $\quad K_H = 6.56 \times 10^{-3}$ g bar^{-1}
Case II: 5.00×10^{-2} g $= (6.56 \times 10^{-3}$ g bar$^{-1}) \times p$

or $\quad p = \dfrac{5.00 \times 10^{-2} \text{ g}}{6.56 \times 10^{-3} \text{ g bar}^{-1}} = 7.62$ bar

7. (i)

$$\underset{\text{Propanone}}{CH_3 - \overset{\overset{O}{\|}}{C} - CH_3} \xrightarrow[\text{(Reduction)}]{NaBH_4, CH_3OH} \underset{\text{Propan-2-ol}}{CH_3 - \overset{\overset{OH}{|}}{CH} - CH_3}$$

$$\xrightarrow[\text{Heat (}-H_2O\text{)}]{\text{Conc. } H_2SO_4} \underset{\text{Propene}}{CH_3CH=CH_2}$$

(ii)

8. (i) In the crystal lattice, transition elements have interstitial vacant spaces into which small sized non-metal atoms such as H, B, C, or N are trapped. These compounds are known as interstitial compounds. These are non-stoichiometric, neither typically ionic nor covalent, *e.g.,* TiC, Mn_4N, Fe_3H, etc.

(ii) As we move from left to right along a transition series (from Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Therefore, atomic volume decreases with increase in atomic mass and hence, density increases.

9. In this cell, electrons will flow from Zn electrode to Cu electrode.
$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(s)}$$

Apply the law of mass action,

$$K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad (\because [Cu_{(s)}] = [Zn_{(s)}] = 1)$$

According to Nernst equation for cell potential,

$$E_{cell} = E°_{cell} - \frac{2.303 RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium E_{cell} is zero.

$$\therefore \quad E°_{cell} = \frac{2.303 RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{2.303 RT}{nF} \log K_c$$

or $\quad \log K_c = \dfrac{n \times 96500}{2.303 \times 8.314 \times 298} \; E°_{cell}$

$$\log K_c = \frac{n}{0.059} \; E°_{cell}$$

$$E°_{cell} = \frac{0.059}{n} \log K_c \quad \text{or } E°_{cell} = \frac{0.059}{2} K_c$$

$$[\because n = 2 \text{ for } Zn^{2+} \text{ and } Cu^{2+} \text{ cell}]$$

10. (i) $[Cr(NH_3)_3(H_2O)_3]Cl_3$
(ii) $[Co(en)_3]_2(SO_4)_3$
(iii) $[Ag(NH_3)_2][Ag(CN)_2]$
(iv) $Hg[Co(SCN)_4]$

OR

Oxidation number of Mn in the complex $= +2$
$\quad$ Mn(25) : [Ar] $3d^5 4s^2$
$\quad$ Mn^{2+} : [Ar] $3d^5$

[Ar] ↑ ↑ ↑ ↑ ↑

Magnetic moment (spin only) of five unpaired electrons in Mn^{2+} is

$$\sqrt{n(n+2)} \quad = \sqrt{5(5+2)} = \sqrt{35} = 5.91 \text{ BM}$$

This is equal to the experimental value given (5.90 BM). Since all the *d*-orbitals are half-filled hence, the only possible geometry is tetrahedral with sp^3 hybridisation.

11. $\rho = \dfrac{Z \times M}{a^3 \times N_A}$ or $Z = \dfrac{\rho \times a^3 \times N_A}{M}$

$$= \frac{(2 \text{ g cm}^{-3})(5 \times 10^{-8} \text{ cm})^3 (6 \times 10^{23} \text{ mol}^{-1})}{75 \text{ g mol}^{-1}} = 2$$

For a metal with $Z = 2$ means that it has body centred cubic *(bcc)* structure. For *bcc* structure,

Atomic radius $(r) = \dfrac{\sqrt{3}}{4} a = \dfrac{\sqrt{3}}{4} \times 5 \text{ Å} = 2.165 \text{ Å}$

$$= 216.5 \text{ pm}$$

12. (i) Tetrafluoroethylene is the monomer that undergoes addition polymerisation to form telfon or polytetrafluoroethylene.

Tetrafluoro ethylene

Polytetra fluoroethylene
(Addition polymer)

(ii) Vinyl chloride is the monomer that undergoes addition polymerisation of form polyvinyl chloride (PVC).

Vinyl chloride

Polyvinyl chloride
(Addition polymer)

(iii) Phthalic acid and ethylene glycol are the monomers that undergo condensation polymerisation to form glyptal.

n HO—CH_2—CH_2—OH + HOOC COOH

Ethylene glycol

n

Phthalic acid

$\downarrow -(2n-1)H_2O$

Glyptal
(Condensation polymer)

13. (i) van't Hoff factor *(i)* is the ratio of normal molecular mass to observed molecular mass or the ratio of observed colligative property to normal colligative property.

When $i > 1$, there is dissociation of solute in the solution.

When $i < 1$, there is association of solute in the solution.

When $i = 1$, there is no association or dissociation of solute in the solution.

(ii) $\pi = iCRT$

or, $0.70 = i \times 0.0103 \times 0.082 \times (27 + 273)$

or, $i = \dfrac{0.70}{0.0103 \times 0.082 \times 300} = 2.76$

Since i is >1 this shows that solute molecules are dissociated in the solution.

14. Reducing sugars are those carbohydrates which can reduce reagents like Tollens' reagent (ammoniacal $AgNO_3$), Benedict's solution and Fehling's solution whereas, non-reducing sugars cannot reduce these reagents.

All monosaccharides whether aldoses or ketoses are reducing sugars.

The characteristic structural feature of reducing sugars is that they must have aldehydic group (—CHO) or ketonic group ($\diagdown C = O$) in the hemiacetal or hemiketal form.

15.
$E°_{cell} = E°_{cathode} - E°_{anode}$
$= -0.40\ V - (-0.74\ V) = + 0.34\ V$
$\Delta_r G° = -nFE°_{cell}$
$= -6 \times 96500\ C\ mol^{-1} \times 0.34\ V$
$= -196860\ C\ V\ mol^{-1} = -196860\ J\ mol^{-1}$
$\Delta_r G° = -2.303\ RT \log K_c$
$-196860 = -2.303 \times 8.314 \times 298 \log K_c$
or $\log K_c = 34.5014$
$K_c = $ Antilog $34.5014 = 3.172 \times 10^{34}$

OR

$E°_{cell} = + 0.80\ V - 0.77\ V = + 0.03\ V$
$\Delta_r G° = -nFE°_{cell}$
$= -(1) \times (96500\ C\ mol^{-1}) \times (0.03\ V)$
$= -2895\ C\ V\ mol^{-1} = -2895\ J\ mol^{-1}$
$\Delta_r G° = -2.303\ RT \log K_c$
$-2895 = -2.303 \times 8.314 \times 298 \times \log K_c$
or $\log K_c = 0.5074$
or $K_c = $ Antilog $(0.5074) = 3.22$

16. (i) 'Cl' in chloroacetic acid shows $-I$ effect which creates less electron density on oxygen of carboxylic acid. Thus, release of proton becomes easier. In case of acetic acid, $+I$ effect of $-CH_3$ group makes the release of proton difficult. Hence, chloroacetic acid is stronger acid than acetic acid. Thus, chloroacetic acid has lower pK_a value than that of acetic acid.

(ii) Carboxylic acids and alcohols both undergo hydrogen bonding among their molecules. Hydrogen bonding among acid molecules is far stronger than among alcohol molecules.

Hence, carboxylic acids have higher boiling points than alcohols.

Strong hydrogen bonding among carboxylic acid molecules (Dimer formation).

(iii) Sodium bisulphite reacts with aldehydes and ketones to form insoluble, crystalline addition products. These products can be easily separated in pure state. These products can be decomposed by dilute mineral acid or alkali to give back original aldehyde or ketone.

Hence, it can be used for purification of aldehydes and ketones.

17. (i) Dehydration will take place and ethene will be formed.

$$CH_3CH_2OH \xrightarrow[600\ K]{Al_2O_3} CH_2=CH_2 + H_2O$$
$$\underset{Ethanol}{} \qquad\qquad \underset{Ethene}{}$$

(ii) Diethylether is formed.

$$2C_2H_5OH \xrightarrow[413\ K]{Conc.\ H_2SO_4} C_2H_5OC_2H_5 + H_2O$$
$$\underset{Ethoxyethane}{}$$

(iii) Phenylethanoate is formed.

18. (i) Physical adsorption is an exothermic process and the equilibrium is represented as
Gas (Adsorbate) + Solid (Adsorbent) ⇌
Gas adsorbed on Solid + Heat
As the temperature is increased, equilibrium shifts in the backward direction, *i.e.,* adsorption decreases (Le Chatelier's principle).

(ii) Brownian movement is due to bombardment of colloidal particles by the molecules of the dispersion medium with unequal forces from different directions. As a result, there is a resultant force acting on them causing the particles to move in zig-zag directions.

(iii) Scattering of light by colloidal particles or Tyndall effect is observed when the diameter of the dispersed particles is not much smaller as compared to the wavelength of the light. So, colloidal particles can scatter light as they have desirable particle size of 10 Å – 10,000 Å.

19. (i) The rate of S_N2 reaction depends on the tendency of leaving group to leave and the tendency of attacking nucleophile to attack. Iodide is a better leaving group because of its larger size than bromide therefore, ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

(ii) (±) 2-butanol is a racemic mixture. It is a mixture which contains two enantiomers in equal proportions and thus, have zero optical rotation. Therefore, it is optically inactive.

(iii) Due to delocalisation of lone pair of electrons of the X atom over the benzene ring, C—X bond in halobenzene acquires some double bond character while in CH_3—X, C—X bond is a pure single bond. Therefore, C—X bond in halobenzene is shorter than in CH_3—X.

20. (i) Silica gel and alumina can act as stationary phase.

(ii) Component C is weakly adsorbed component thus, travels faster than A and B components with mobile phase and hence, eluted first.

(iii) Different components of the mixture are adsorbed at different rates on the surface of adsorbent. Thus, in mobile phase each component move on stationary phase to different levels and get separated.

21. (i) Ionisation isomerism : When two complexes have same molecular formula but give different ions in solution, they are said to be ionisation isomers and the phenomenon is known as ionisation isomerism. This isomerism arises due to the exchange of ions between coordination sphere and ionisation sphere. For example,
$[Co(NH_3)_5Br]SO_4$ and
Pentaamminebromidocobalt(III)
$[Co(NH_3)_5SO_4]Br$
Pentaamminesulphatocobalt(III) bromide

(ii) Linkage isomerism : When any monodentate ligand in a complex has more than one donor atoms, it may be bonded to metal ion through either of the atoms and gives different isomers. For example, ligand SCN^- may be bonded to the metal either through sulphur or through nitrogen to give two different isomers.

$[Co(NH_3)_5SCN]Cl_2$ and $[Co(NH_3)_5NCS]Cl_2$
Pentaamminethiocyanato   Pentaammineisothiocyanato
cobalt(III) chloride   cobalt(III) chloride

(iii) Coordination isomerism : This type of isomerism arises when both positive and negative ions of a compound are complex ions. There may be an exchange of ligand molecules between the two coordination spheres of two ions to give two coordination isomers.

$[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
Tetraamminecopper(II)   Tetraammineplatinum(II)
tetrachloridoplatinate(II)   tetrachloridocuprate(II)

22. (i) The electronic configuration of Ce $(Z = 58)$ is $_{58}Ce = [Xe]\ 4f^1 5d^1 6s^2$

Cerium can lose four electrons $(4f^1 5d^1 6s^2)$ in aqueous solution to acquire stable configuration of rare gas xenon. Due to small size and high charge, Ce^{4+} ion has high hydration energy

(ii) The second and third members in each group of transition elements have very similar atomic radii due to lanthanoid contraction which arises due to poor shielding effect of f-electrons.

(iii) (a)   (b)

23. (i) Detergents get accumulated in the river water causing foaming in river and thus, water gets polluted and becomes unfit for drinking.

(ii) Leadership, awareness and concern for people and environment, are the values displayed by Shyam.

(iii) Detergents are mainly classified into three categories :

(a) Anionic detergents, which are sodium salts of sulphonated long chain alcohols or hydrocarbons.

(b) Cationic detergents, which are quarternary ammonium salts of acetates, chlorides or bromides as anions.

(c) Non-ionic detergents which do not contain any ion in their constitution.

24 (i) $a \propto P_0$ and $(a - x) \propto P_t$

Hence, $k = \dfrac{2.303}{t} \log \dfrac{P_0}{P_t}$ (P_t = pressure of Cl_2O_7 at time t)

(a) $t = 50$ s, $P_0 = 0.062$ atm, $P_t = 0.044$ atm

$k = \dfrac{2.303}{50\ \text{s}} \log \dfrac{0.062\ \text{atm}}{0.044\ \text{atm}} = 6.86 \times 10^{-3}\ \text{s}^{-1}$

(b) $t = 100$ s, $P_t = ?$, $k = 6.86 \times 10^{-3}\ \text{s}^{-1}$

$6.86 \times 10^{-3}\ \text{s}^{-1} = \dfrac{2.303}{100\text{s}} \log \dfrac{0.062\ \text{atm}}{P_t}$

$\log \dfrac{0.062}{P_t} = 0.2979$

$\Rightarrow \dfrac{0.062}{P_t}$ = Antilog 0.2979 = 1.986

or $P_t = 0.0312$ atm

(ii) $k = \dfrac{2.303}{t} \log \dfrac{a}{a-x} = \dfrac{2.303}{32\,\text{min}} \log \dfrac{a}{a - a/4}$

$= \dfrac{2.303}{32} \log \dfrac{4}{3}\ \text{min}^{-1} = 0.009\ \text{min}^{-1}$

$t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{0.009} = 77$ min

OR

(i) Average rate of reaction is obtained by dividing the change in concentration of a particular species by the time interval. As the concentration changes are not uniform, the average rate does not give a true picture of the reaction rate.

(ii) Coal dust has greater surface area than a lump of coal. Thus, coal dust has greater ease of coming in contact with air and therefore burns explosively.

(iii) Water boils at temperature lower than 100°C due to low atmospheric pressure at higher altitudes. Thus, when eggs or rice are boiled in water at higher altitudes, the water boils earlier *i.e.,* at lower temperature. Hence, to cook the food completely the food should be heated for more time.

(iv) At room temperature, there is no reaction between hydrogen and oxygen as the activation energy of the reaction is very high. They require very high temperature to react which can be produced generally by electric spark or explosion.

(v) Consider the reaction
$A + B \rightarrow C$
Then, according to rate law,
Rate = $k [A]^x [B]^y$
where k = rate constant
$[A]$ and $[B]$ are concentrations of A and B and x and y are the order of the reaction w.r.t. A and B respectively.

Now, as the concentration of *A* and *B* changes, the rate of reaction changes such that rate constant remains unchanged. Thus, rate constant of a reaction does not depend on the concentration of the reactants.

25. **(i)** (a) $H_2O > H_2Te > H_2Se > H_2S$

   Because the boiling points of hydride increase with the increase in molecular mass of the elements. H_2O has exceptionally high boiling point because of intermolecular hydrogen bonding.

   (b) $NH_3 > PH_3 > AsH_3 > SbH_3$

   With the increase in size of the metal, the electron density of the lone pair gets diffused over a large region and ability to donate lone pair gets reduced hence, basic character decreases.

(ii) (a) In bismuth, due to inert pair effect only $6p^3$ electrons are used, thus Bi^{3+} is formed and Bi^{5+} does not exist (except in BiF_5). However, in phosphorus, $3s^2$ and $3p^3$ electrons can take part in bonding thus, P^{5+} can exist.

   (b) Nitrogen has a strong tendency to form $p\pi$-$p\pi$ multiple bonds between N and O atoms and thus, it forms number of oxides which have no P, As, Sb or Bi analogues as these elements of group 15 do not have tendency to form $p\pi$-$p\pi$ multiple bonds.

   (c) In hydrogen fluoride, strong intermolecular hydrogen bonding is present, due to small size and high electronegativity of fluorine and hence, HF is a liquid having higher boiling point than HCl which is a gas due to the absence of hydrogen bonding.

OR

(i) (a) For spontaneity of a reaction, ΔG must be negative. Decomposition of O_3 is an exothermic process ($\Delta H = $ –ve) and occurs with increase in entropy ($\Delta S = $ +ve). These two effects reinforce each other which results in large negative Gibbs energy change according to the relation,

$$\Delta G = \Delta H - T\Delta S$$

Thus, its decomposition is a spontaneous reaction.

(b) In SF_6, S is surrounded by $6\,F^-$ octahedrally. Therefore, attack of water molecule on S is sterically hindered. Hence, it is an inert substance.

(c) In a group, on moving down the group there is decrease in *E*–H bond dissociation enthalpy which increases acidic character. Thus, H_2S is less acidic than H_2Te.

(d) SO_2 is water soluble therefore, it dissolves in rain water causing acid rain. Moreover, when released in air, it leads to several diseases like eye irritation, redness in eyes, asthma, bronchitis, etc. Thus, it is considered as an air pollutant.

(ii) When white phosphorus is heated with conc. NaOH solution in an inert gas atmosphere, phosphine gas is produced.

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Phosphine}}{PH_3} + 3NaH_2PO_2$$

26. **(i)** (a) Since (*A*) releases N_2 with nitrous acid, it must be a primary amine.

$$\underset{A}{C_9H_{11}NH_2} \xrightarrow{HNO_2} \underset{B}{C_9H_{11}OH} + N_2$$

(b) The alcohol *(B)* is optically active, therefore, it should contain a chiral carbon atom. Keeping in view, the molecular formula of *(A)* and *(B)* as well as the fact that *(B)* on oxidation gives a dicarboxylic acid, *i.e.,* has two side chains on the benzene ring, the compound *(B)* can be

(c) Since the dicarboxylic acid on heating forms an anhydride, the two side chains as well as the two –COOH groups are at *ortho*-position to each other, *i.e.,*

The reactions can be explained as follows :

(A)

Optically active
(B)

Phthalic acid   Phthalic anhydride

(ii) (a) Gabriel phthalimide reaction involves the nucleophilic attack of the phthalimide anion on organic halogen compound.

Alkyl halide

Due to resonance in aryl halides, there is some double bond character in Ar – X because of which it is difficult to break. Therefore, aryl halides do not undergo nucleophilic substitution reactions easily and aromatic primary amines cannot be prepared by Gabriel synthesis.

+ Ar — X →×→ No reaction

(b) Tertiary amines do not undergo acylation reaction because they do not have hydrogen attached to nitrogen.

OR

(i) The final product is an *ortho*-substituted monocarboxylic acid. Therefore, it is monocarboxylic aromatic acid with chloro group at the *ortho*-position. Therefore, it is

Thus, the sequence of the reactions can be visualised as follows :

Toluene   o-Nitrotoluene
(A)   (B)

o-Toluidine   o-Toluenediazonium
(C)   chloride

o-Chlorotoluene   o-Chlorobenzoic
(D)   acid

(ii) $CH_3CN + H_2O \xrightarrow{NaOH} CH_3CONH_2$

Br_2 + aq. KOH $\Big|$ Hoffmann bromamide reaction

$CH_3NH_2 \leftarrow$

□□□

Directions : In the following questions, a statement of Assertion is followed by a statement of Reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

PHYSICAL CHEMISTRY

1. **Assertion :** Atoms can neither be created nor be destroyed.
    Reason : Under similar conditions of temperature and pressure, equal volume of gases does not contain equal number of atoms.

2. **Assertion :** ZnO turns yellow on heating.
    Reason : This is due to the defect similar to Frenkel defect.

3. **Assertion :** Spontaneous process is an irreversible process and may be reversed by some external agency.
    Reason : Decrease in enthalpy is a contributory factor for spontaneity.

4. **Assertion :** If 100 cc of 0.1 N HCl is mixed with 100 cc of 0.2 N HCl, the normality of the final solution will be 0.30.
    Reason : Normalities of similar solutions like HCl can be added.

5. **Assertion :** $E°_{cell}$ should have a positive value for the cell to function.
    Reason : $E°_{cathode} < E°_{anode}$

6. **Assertion :** The pH of NH_4Cl solution in water is less than 7 and pH of CH_3COONa solution is more than 7.
    Reason : NH_4Cl is a salt of weak base NH_4OH and strong acid HCl whereas CH_3COONa is a salt of weak acid CH_3COOH and strong base NaOH.

7. **Assertion :** For an elementary reaction, order of reaction is equal to its molecularity, provided pressure or concentration remains constant.
    Reason : By changing temperature and pressure, reaction may not remain an elementary reaction.

8. **Assertion :** At low pressure, the van der Waals' equation is reduced to $Z = 1 + \dfrac{aP}{RT}$.
    Reason : At low pressure, molar volume is low so b can be neglected.

9. **Assertion :** Coagulation power of Al^{3+} is more than Na^+.
    Reason : Greater the valency of the flocculating ion added, greater is its power to cause precipitation (Hardy Schulze rule).

10. **Assertion :** Equivalent weight of NH_3 in the reaction $N_2 \rightarrow NH_3$ is 17/3 while that of N_2 is 28/6.
    Reason : Equivalent weight
    $$= \frac{\text{Molecular weight}}{\text{Number of } e^- \text{ lost or gained per mole of reactant}}$$

ORGANIC CHEMISTRY

11. **Assertion :** Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.
    Reason : This reaction proceeds through the formation of a carbocation.

12. **Assertion :** A mixture of *o*-nitrophenol and *p*-nitrophenol can be separated by steam distillation.
Reason : *o*-Nitrophenol is steam volatile but *p*-nitrophenol is not though both are insoluble in water.

13. **Assertion :** Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.
Reason : The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO_2^+.

14. **Assertion :** Mixture of benzaldehyde and acetaldehyde in hot alkaline medium gives cinnamaldehyde.
Reason : Benzaldehyde is stronger electrophile than acetaldehyde.

15. **Assertion :** Alcohols react both as nucleophiles and electrophiles.
Reason : Alcohols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides and hydrogen.

16. **Assertion :** All the hydrogen atoms in $CH_2{=}C{=}CH_2$ lie in one plane.
Reason : All the carbon atoms in it are sp^2 hybridised.

17. **Assertion :** Both aliphatic and aromatic secondary amines react with HNO_2 to give *N*-nitrosoamines which on warming with a crystal of phenol and a few drops of conc. H_2SO_4 form a green solution which on making alkaline with aq. NaOH turns deep blue and then red on dilution.
Reason : This reaction is called Liebermann's nitroso reaction and is used as a test for secondary amines.

18. **Assertion :** *D*(+)–Glucose is dextrorotatory in nature.
Reason : '*D*' represents its dextrorotatory nature.

19. **Assertion :** 1,3-Butadiene is the monomer for natural rubber.
Reason : Natural rubber is formed through anionic addition polymerisation.

20. **Assertion :** Chemicals added to foods for increasing their shelf life are called preservatives.
Reason : Natural sweeteners like sucrose and artificial sweeteners like saccharin are commonly used as food preservatives.

INORGANIC CHEMISTRY

21. **Assertion :** O_2 molecule is diamagnetic while C_2 molecule is paramagnetic in nature.
Reason : Bond order of O_2 molecule is 1.5 and that of C_2 molecule is 2.5.

22. **Assertion :** Hydrometallurgy involves dissolving the ore in a suitable reagent followed by precipitation by a more electropositive metal.
Reason : Copper is extracted by hydrometallurgy.

23. **Assertion :** Mg is not present in enamel of human teeth.
Reason : Mg is an essential element for biological functions of human.

24. **Assertion :** Heavy water has slightly higher values of physical constants like b.p., m.p., density, viscosity etc. than water.
Reason : Heavy water has higher molecular mass as compared to ordinary water.

25. **Assertion :** SO_2 is polar (μ = 1.60 D) while SO_3 is non-polar (μ = 0 D) although S in both of them is sp^2-hybridised.
Reason : SO_2 has a bent structure while SO_3 has trigonal planar structure.

26. **Assertion :** $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.
Reason : *d-d* transition is not possible in $[Sc(H_2O)_6]^{3+}$.

27. **Assertion :** Actinoids form relatively less stable complexes as compared to lanthanoids.
Reason : Actinoids cannot utilise their $5f$ orbitals in bonding similar to lanthanoids which do not use their $4f$ orbitals for bonding.

28. **Assertion :** Diamond and graphite do not have the same crystal structure.
Reason : Diamond is crystalline while graphite is amorphous.

29. **Assertion :** Hydrogen and deuterium are both present in ordinary dihydrogen.
Reason : Heavy hydrogen or deuterium was separated from liquid hydrogen by fractional distillation by H.C. Urey.

30. **Assertion :** PCl_5 is covalent in gaseous and liquid states but ionic in solid state.
Reason : PCl_5 in solid state consists of tetrahedral PCl_4^+ cation and octahedral PCl_6^- anion.

SOLUTIONS

1. (c) : Atoms can neither be created nor be destroyed. This is the statement of law of conservation of mass.

Under similar conditions of temperature and pressure, equal volume of gases contains equal number of atoms.

As, $PV = nRT$ (Ideal gas equation)

If, for I case, $P_1 V_1 = n_1 R T_1$

for II case, $P_2 V_2 = n_2 R T_2$

$$\Rightarrow \quad \frac{P_1 V_1}{P_2 V_2} = \frac{n_1 R T_1}{n_2 R T_2}$$

For $P_1 = P_2$, $V_1 = V_2$ and $T_1 = T_2$

$\Rightarrow n_1 = n_2$

2. (b) : ZnO loses oxygen on heating.

$$ZnO \longrightarrow Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

And the excess of Zn^{2+} ions thus produced get trapped into the vacant interstitial sites and the electrons in the neighbouring interstitial sites. These electrons absorb some energy of the white light and emit yellow colour.

This defect is similar to Frenkel defect and is found in crystals having Frenkel defects.

3. (b)

4. (d) : If 100 cc of 0.1 N HCl is mixed with 100 cc of 0.2 N HCl, the normality of the final solution will be 0.15.

$$N_1 V_1 + N_2 V_2 = N_3 V_3$$

i.e., $0.1 \times 100 + 0.2 \times 100 = N_3 \times 200$

or $N_3 = \frac{0.3 \times 100}{200} = 0.15$ N

5. (c) : For a cell to function, $\Delta G°$ should be negative.

$\Delta G° = -nFE°_{cell}$

For $\Delta G°$ to be negative, $E°_{cell}$ should be positive.

$E°_{cell} = E°_{cathode} - E°_{anode}$

To have positive value of $E°_{cell}$, $E°_{cathode} > E°_{anode}$.

6. (a)

7. (a) : For an elementary reaction, order of reaction is equal to its molecularity. But if the conditions of pressure or concentration are changed, order and molecularity may not remain same as in that case the reaction may not remain an elementary reaction but may become a complex reaction.

8. (d) : For n moles of a real gas, van der Waals' equation is given by

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\Rightarrow \left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$[\because \text{Molar volume } (V_m) = V/n]$$

At low pressure, $V_m >> b$

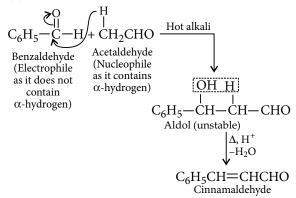$$\therefore \left(P + \frac{a}{V_m^2}\right)V_m = RT$$

$$PV_m + \frac{a}{V_m} = RT \Rightarrow \frac{PV_m}{RT} = 1 - \frac{a}{V_m RT}$$

$$\therefore Z = 1 - \frac{aP}{RT} \qquad \left[\because Z = \frac{PV_m}{RT} \text{ and } V_m \propto \frac{1}{P}\right]$$

9. (a)

10. (a) : $\overset{0}{N_2} + 6e^- \rightarrow 2N^{3-}$

$$\therefore \text{Equivalent weight of } NH_3 = \frac{14 + 3}{3} = \frac{17}{3}$$

(Mol. wt. of $NH_3 = 17$)

While equivalent weight of $N_2 = \frac{14 \times 2}{6} = \frac{28}{6}$.

11. (c) : The reaction follows S_N2 mechanism which does not proceed through a carbocation.

12. (a) : Steam distillation is used for separation of those organic compounds which (i) are insoluble in water. (ii) are volatile with steam (iii) possess a high vapour pressure at 373 K and (iv) contain non-volatile impurities.

13. (a)

14. (a) : This is a Claisen-Schmidt reaction.

$$\underset{\substack{\text{Benzaldehyde} \\ \text{(Electrophile} \\ \text{as it does not} \\ \text{contain} \\ \alpha\text{-hydrogen)}}}{C_6H_5 - \overset{O}{\underset{}{C}} - H} + \underset{\substack{\text{Acetaldehyde} \\ \text{(Nucleophile} \\ \text{as it contains} \\ \alpha\text{-hydrogen)}}}{CH_2CHO} \xrightarrow{\text{Hot alkali}}$$

$$\underset{\text{Aldol (unstable)}}{C_6H_5 - CH - \overset{\boxed{OH \quad H}}{CH} - CHO}$$

$$\downarrow \Delta, H^+ \quad -H_2O$$

$$\underset{\text{Cinnamaldehyde}}{C_6H_5CH = CHCHO}$$

15. (b) : Alcohols as nucleophiles :

$$R-\overset{..}{\underset{..}{O}}-H + \overset{+}{C}- \longrightarrow R-\overset{\overset{H}{|}}{\underset{..}{O}}-\overset{|}{\underset{|}{C}}-$$

$$\longrightarrow R-\overset{..}{\underset{..}{O}}-\overset{|}{\underset{|}{C}}- + H^+$$

Alcohols as electrophiles :
The bond between C—O is broken. Protonated alcohols react in this manner and act as electrophiles.

$$R-CH_2-\overset{..}{\underset{..}{O}}H + H^+ \longrightarrow R-CH_2\overset{+}{\underset{Br^-}{-}}OH_2$$

$$R-CH_2-Br + H_2O$$

16. (d) : The two hydrogen atoms on first carbon and the two hydrogen atoms on the third carbon atom lie in perpendicular planes. The central carbon atom is sp-hybridised while terminal carbon atoms are sp^2-hybridised.

17. (b) : The reaction involved is represented as
$(CH_3CH_2)_2NH + HONO \longrightarrow$
  Diethylamine

$$(CH_3CH_2)_2N-N=O + H_2O$$
N-Nitrosodiethylamine (yellow oil)

On heating with acid, they give back 2° amines.
$R_2N-NO + HCl \longrightarrow R_2NH + NOCl$
Nitrosoamines on warming with phenol and a few drops of conc. H_2SO_4 give a brown or red colour which soon changes to blue green. The colour changes to red on dilution and further changes to blue or violet with alkali. This colour change is referred to Liebermann's nitroso reaction and is used for the test of 2° amines.

18. (c) : 'D' corresponds to the position of —OH group on the right side on the farthest asymmetric C-atom.

19. (d) : Isoprene (2-methyl-1,3-butadiene) is the monomer of natural rubber.
Natural rubber is formed through cationic addition polymerisation. Cationic addition polymerisation is catalysed by acids and Lewis acids. Alkenes containing electron-donating groups usually undergoes cationic addition polymerisation.

$$n CH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH_2 \xrightarrow{\text{Polymerisation}}$$

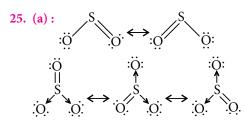$$\left(CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\right)_n$$

20. (c) : Sweetness are added to impart sweetness to the food. Sodium benzoate, table salt, are some commonly used preservatives.

21. (d) : $O_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$
$$(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^1 = \pi^* 2p_y^1)$$
Bond order $= \dfrac{1}{2}(N_b - N_a) = \dfrac{1}{2}(10-6) = 2$
It contains two unpaired electrons hence it is paramagnetic in nature.
$C_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$
Bond order $= \dfrac{1}{2}(8-4) = 2$
All electrons are paired hence it is diamagnetic in nature.

22. (b) : In hydrometallurgy, metal ore is dissolved in a suitable reagent then a more electropositive metal displaces the pure metal which is extracted.

23. (b) : Enamel $[Ca_3(PO_4)_2 \cdot CaF_2]$ the hardest substance of the body is composed of fluorine not magnesium. Magnesium is an essential element as it acts as a cofactor of many enzymes of glycolysis and a number of other metabolic reactions.

24. (a) : The molecular mass of H_2O and D_2O are 18.015 and 20.0276 g mol^{-1} respectively.

25. (a) :

26. (a) : $[Sc(H_2O)_6]^{3+}$ has no unpaired electron in its d subshell and thus d-d transition is not possible whereas $[Ti(H_2O)_6]^{3+}$ has one unpaired electron in its d subshell which gives rise to d-d transition to impart colour.

27. (d) : Actinoids are more reactive and show greater range of oxidation states and can utilise their $5f$-orbitals along with $6d$-orbitals in bonding.

28. (c) : In diamond, C-atoms are sp^3 hybridised while in graphite, they are sp^2 hybridised.

29. (b)

30. (a) : PCl_5 is trigonal bipyramidal containing sp^3d hybridised P atom in liquid and gaseous states whereas in solid state it consists of tetrahedral PCl_4^+ cation and octahedral PCl_6^- anion. ◈◈
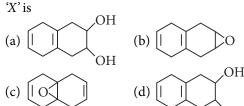
OLYMPIAD PROBLEMS

1. Select the correct ground state electronic configuration of the element which is just above the element with atomic number 47 in the same periodic group.
   (a) [Ar] $3d^9, 4s^2$
   (b) [Ar] $3d^{10}, 4s^2$
   (c) [Ar] $3d^{10}, 4s^1$
   (d) [Kr] $4d^{10}, 5s^1$

2. In the radioactive decay $^{232}_{92}X \longrightarrow ^{220}_{89}Y$, how many α- and β-particles are ejected from X to form Y?
   (a) 5 α and 5 β
   (b) 3 α and 3 β
   (c) 3 α and 5 β
   (d) 5 α and 6 β

3. A nucleophile must necessarily have
   (a) an overall +ve charge
   (b) an overall –ve charge
   (c) an unpaired electron
   (d) a lone pair of electrons.

4. Consider the following changes :
   1. Sublimation energy of $M = p$
   2. Sublimation energy + $I.E._1$ + $I.E._2$ of $M = q$
   3. $I.E._1$ of $M = r$
   4. $I.E._2$ of $M = s$
   5. $I.E._1$ + $I.E._2$ of $M = t$
   The enthalpy change for the reaction, $M^+_{(g)} \longrightarrow M^{2+}_{(g)} + e^-$ could be calculated from the energy value associated with
   (a) $(p) + (r) + (s)$
   (b) $(q) - (p) + (r)$
   (c) $(p) + (t)$
   (d) $(t) - (r)$

5. The wavelength of the third line of the Balmer series for a hydrogen atom is
   (a) $\dfrac{21}{100\, R_H}$
   (b) $\dfrac{100}{21\, R_H}$
   (c) $\dfrac{21\, R_H}{100}$
   (d) $\dfrac{100\, R_H}{21}$

6. In the following reaction,

    $\xrightarrow[\text{(1 mole)}]{m\text{-CPBA}}$ X (Major product)

   'X' is
   (a)
   (b)
   (c)
   (d)

7. The electrolysis of carnallite (KCl·MgCl₂·6H₂O) yields
   (a) potassium ions
   (b) magnesium ions
   (c) magnesium and chlorine
   (d) potassium and chlorine.

8. The number of moles of AgI, which may be dissolved in 1.0 L of 1.0 M CN⁻ solution is
   (K_{sp} for AgI = 1.2×10^{-17} M² and
   K_c for [Ag(CN)₂]⁻ = 7.1×10^{19} M⁻²)
   (a) 0.42
   (b) 0.30
   (c) 0.49
   (d) 0.31
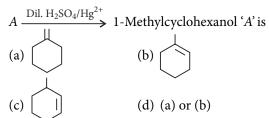
9. The major product obtained in the given reaction is
   $NC-CH=CH_2 \xrightarrow{HBr}$
   (a) $NC-\underset{\underset{Br}{|}}{CH}-CH_3$
   (b) $NC-CH_2-CH_2Br$
   (c) an equimolar mixture of (a) and (b)
   (d) none of these.

10. Select the correct statement for BrF₅.
    (a) All fluorine atoms are in same plane.
    (b) Four fluorine atoms and bromine atom are in the same plane.
    (c) Four fluorine atoms are in the same plane.
    (d) All F—Br—F bond angles are equal to 90°.

11. A chemical reaction is spontaneous at 298 K but non-spontaneous at 350 K. Which one of the following is true for the reaction?

$$\Delta G \quad \Delta H \quad \Delta S$$
(a) $\quad$ – $\quad$ – $\quad$ +
(b) $\quad$ + $\quad$ + $\quad$ +
(c) $\quad$ – $\quad$ + $\quad$ –
(d) $\quad$ – $\quad$ – $\quad$ –

12. In the reaction,

$A \xrightarrow{\text{Dil. H}_2\text{SO}_4/\text{Hg}^{2+}}$ 1-Methylcyclohexanol 'A' is

(a) [structure]   (b) [structure]

(c) [structure]   (d) (a) or (b)

13. CO_3^{2-} and SO_3^{2-} can be distinguished from each other by using
(a) baryta water
(b) limewater
(c) acidified dichromate
(d) sulphamic acid.

14. The first order rate constant for hydrolysis of a certain insecticide in water at 12°C is 1.45 yr^{-1}. A quantity of this insecticide is washed into a lake in June, leading to an overall concentration of 5.0×10^{-7} g/cm^3 of water. Assuming that the effective temperature of the lake is 12°C, what will be the concentration of the insecticide in June of the following year?
(a) 7×10^{-8} g/cm^3
(b) 4.2×10^2 g/cm^3
(c) 1.2×10^{-7} g/cm^3
(d) 5.6×10^2 g/cm^3

15. Which of the following alkyl halides would give the highest yield of substitution products under conditions favourable to a bimolecular reaction?
(a) $CH_3CH_2CH_2CH_2CH_2Br$
(b) $CH_3CH_2CH_2CH-CH_3$
     $\quad\quad\quad\quad\quad\quad |$
     $\quad\quad\quad\quad\quad\quad Br$
(c) $CH_3CH_2-CH-CH_2Br$
     $\quad\quad\quad\quad\quad |$
     $\quad\quad\quad\quad\quad CH_3$
(d) $CH_3CH_2-C-CH_3$
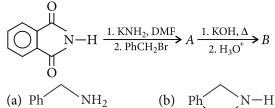 $\quad\quad\quad\quad | \;(Br)$
     $\quad\quad\quad\quad CH_3$

16. Which of the following is incorrect distribution of electrons in d-orbitals of metal in corresponding complexes?
(a) $[NiCl_4]^{2-}$

(b) $[Ni(NH_3)_6]^{2+}$

(c) $[Co(H_2O)_6]^{2+}$

(d) $[Co(SCN)_4]^{2-}$
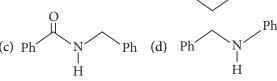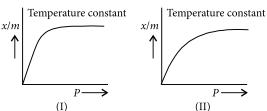
17. How much charge is required to produce hydrogen gas at the rate of 1 mL s^{-1} by the electrolysis of molten NaCl?
(a) 8.6 C
(b) 18.4 C
(c) 4.3 C
(d) 1.4 C

18. The end product 'B' of the given reaction is

[structure] $N-H \xrightarrow[\text{2. PhCH}_2\text{Br}]{\text{1. KNH}_2, \text{DMF}} A \xrightarrow[\text{2. H}_3\text{O}^+]{\text{1. KOH, }\Delta} B$

(a) Ph$\diagdown$NH$_2$
(b) Ph$\diagdown$N$-$H
(c) Ph$\diagdown$C(=O)$-$N(H)$\diagdown$Ph
(d) Ph$\diagdown$N(H)$\diagdown$Ph
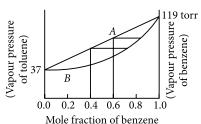
19. A mixed oxide of iron, Fe_3O_4 is represented by
(a) $Fe_2^{II}Fe^{III}O_4$
(b) $Fe^{III}(Fe^{II}Fe^{III})O_4$
(c) $Fe_2^{II}Fe^{II}O_4$
(d) none of these.

20. Observe the given graphs and mark the correct statement.

(a) (I) represents Freundlich's adsorption isotherm while (II) represents Langmuir's adsorption isotherm.
(b) (I) represents Langmuir's adsorption isotherm while (II) represents Freundlich's adsorption isotherm.
(c) Both Freundlich's and Langmuir's adsorption isotherms have been found to be applicable in the adsorption of gases on the solids only.

(d) Change of pressure affects a lot and further adsorption can take place in both the isotherms.

21. The presence of a primary alcoholic group ($-CH_2OH$) in glucose is inferred by
   (a) its oxidation by bromine water to give gluconic acid [$HOOC(CHOH)_4CH_2OH$], which on further oxidation with concentrated HNO_3 yields glucaric acid
   (b) the fact that a solution of glucose in an inert solvent becomes effervescent upon the introduction of sodium.
   (c) the fact that a solution of glucose becomes coloured upon the addition of $FeCl_3$
   (d) its reaction with the Tollens' reagent.

22. Solution of which of the following compounds does not give sulphide precipitate on passing H_2S gas?
   (a) $CuSO_4$ (b) $CdSO_4$
   (c) $K_3[Cu(CN)_4]$ (d) $K_2[Cd(CN)_4]$

23. Observe the given graph :

Choose the correct option.
   (a) A represents vapour composition and B represents liquid composition.
   (b) Both A and B represent liquid composition.
   (c) Both A and B represent vapour composition.
   (d) A represents liquid composition and B represents vapour composition.

24. Compound 'X' gives following reactions :

Its structure can be

25. Which of the given metal ion(s) have aqueous chemistry?
   (a) Sm^{2+} (b) Eu^{2+}
   (c) Yb^{2+} (d) All of these

26. Sulphide ion in alkaline solution reacts with solid sulphur to form polysulphide ions having formulae S_2^{2-}, S_3^{2-}, S_4^{2-} and so on. The equilibrium constant for the formation of S_2^{2-} is 12 and for the formation of S_3^{2-} is 130, both from S and S^{2-}. What is the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S?
   (a) 10.8   (b) – 0.092
   (c) 15.60   (d) None of these

27. The ease of reduction of C_6H_5COCl (I), C_6H_5CHO (II),
$$C_6H_5-\overset{\overset{O}{\|}}{C}-OC_2H_5 \text{ (IV)}$$
$C_6H_5COCH_3$ (III) and by hydrogen over a palladium catalyst follows the order
   (a) I > II > III > IV   (b) IV > III > II > I
   (c) II > III > I > IV   (d) III > II > I > IV

28. Main source of lead is PbS. It is converted to Pb by
   (I) $PbS \xrightarrow[\Delta]{Air} PbO + SO_2 \xrightarrow{C} Pb + CO_2$
   (II) $PbS \xrightarrow[\Delta]{Air} PbO + PbS \xrightarrow{PbS} Pb + SO_2$
   Self reduction process is
   (a) I   (b) II
   (c) both (I) and (II)   (d) none of these.

29. How many octahedral sites per sphere are there in a cubic close-packed structure?
   (a) Four (b) Two   (c) One   (d) Six

30. The acid strengths of the following decrease in the order
   (a) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$
   (b) $CH_3COOH > CH_2ClCOOH > CHCl_2COOH > CCl_3COOH$
   (c) $CCl_3COOH > CH_3COOH > CH_2ClCOOH > CHCl_2COOH$
   (d) $CH_2ClCOOH > CHCl_2COOH > CCl_3COOH > CH_3COOH$

ANSWER KEYS

1. (c)	2. (b)	3. (d)	4. (d)	5. (b)
6. (c)	7. (c)	8. (c)	9. (b)	10. (c)
11. (d)	12. (d)	13. (c)	14. (c)	15. (a)
16. (d)	17. (b)	18. (a)	19. (b)	20. (b)
21. (a)	22. (c)	23. (d)	24. (c)	25. (d)
26. (a)	27. (a)	28. (b)	29. (c)	30. (a)

◈◈

CONCEPT BOOSTER

Dear all!! Exam season is coming. As a mentor it is my duty to show you the acute areas of chemistry involved in competitive examinations. With this view I am presenting this article on reduction and selective reduction. I hope you will like it. If my experience works in favour of you all, I will be the happiest person. Do take care.

*Arunava Sarkar

MYSTERY OF REDUCTION

Some Common Aspects

- Aldehyde $\xrightarrow{[H]}$ Alcohol $\xrightarrow{[H]}$ Alkane
- Ketone $\xrightarrow{[H]}$ Alcohol $\xrightarrow{[H]}$ Alkane
- Alcohol $\xrightarrow{[H]}$ Alkane
- Cyanide $\xrightarrow{[H]}$ 1° Amine
- Isocyanide $\xrightarrow{[H]}$ 2° Amine
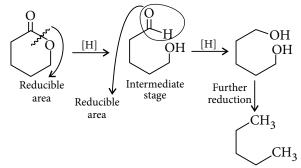- Acid chloride $\xrightarrow{[H]}$ Aldehyde $\xrightarrow{[H]}$ Alcohol $\xrightarrow{[H]}$ Alkane

In case of Rosenmund reduction, reaction can be stopped at aldehydic stage.

- Ester $\xrightarrow{[H]}$ Alcohol $\xrightarrow{[H]}$ Alkane
- Cyclic ether $\xrightarrow{[H]}$ Alcohol $\xrightarrow{[H]}$ Alkane
  (1° or 2°)
- Nitro compound $\xrightarrow{[H]}$ Nitroso $\xrightarrow{[H]}$ Hydroxyl amine $\xrightarrow{[H]}$ 1° Amine
- Alkyl isocyanate $\xrightarrow{[H]}$ $[R-NH-CH_2-OH]$
  ($R-N=C=O$) $\xrightarrow{[H]}$ 2° Amine
- Oxime $\xrightarrow{[H]}$ 1° Amine

$$\begin{array}{c} R_1 \\ R_2 \end{array} C = N - OH \xrightarrow{4[H]} \begin{array}{c} R_1 \\ R_2 \end{array} CH-NH_2 + H_2O$$
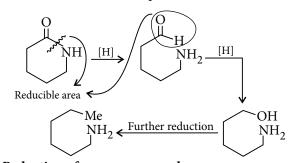
- **Reduction of lactone (cyclic ester) :**

- **Reduction of lactam (cyclic amide) :**
  It is almost similar to the previous one.

- **Reduction of azoxy compounds :**
  Take the example of aryl azoxy compounds.

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- **Reduction of triple bond :**

  In stepwise reduction, triple bond at first gets converted to double bond and finally to single bond.

  $$R_1—C{\equiv}C—R_2 \xrightarrow{2[H]} R_1—CH{=}CH—R_2 \xrightarrow{2[H]}$$
  $$\underset{\text{Triple bond (Alkyne)}}{} \quad \underset{\text{Double bond (Alkene)}}{}$$
  $$\underset{\text{Single bond (Alkane)}}{R_1—CH_2—CH_2—R_2} \longleftarrow$$

- **Reduction of double bond :**

  $$\underset{\text{(Alkene)}}{R_1—CH{=}CH—R_2} \xrightarrow{2[H]} \underset{\text{(Alkane)}}{R_1—CH_2—CH_2—R_2}$$

- **Reduction of halide compounds :**

  $$\underset{\substack{[H]\ \ [H]\\ \text{Aliphatic halide}}}{R{\overset{..}{-}}X} \xrightarrow{2[H]} RH + HX \ ; \ \underset{\substack{\text{Aromatic}\\ \text{halide}}}{ArX} \xrightarrow{2[H]} ArH + HX$$

- **Reduction of carboxylic acids :**

  $$\underset{\substack{\text{(Carboxylic}\\ \text{acid)}}}{RCOOH} \xrightarrow[(-H_2O)]{2[H]} \underset{\text{(Aldehyde)}}{R—CHO} \xrightarrow{2[H]} \underset{\text{(1° Alcohol)}}{R—CH_2OH}$$

  $$\underset{}{R—CH_3} \xleftarrow[(-H_2O)]{2[H]}$$

- **Reduction of alkyl or aryl azide compounds :**

  $$R—\overset{..}{\underset{..}{N}}{=}\overset{+}{N}{=}\overset{..}{\underset{..}{N}} \xrightarrow{\Delta} R—\overset{..}{\underset{..}{N}}{-}\overset{+}{N}{\equiv}N \xrightarrow[-N_2]{\Delta} \underset{\text{Nitrene}}{R—\overset{..}{\underset{..}{N}}} \xrightarrow{2[H]}$$

  $$\underset{\text{1° Amine}}{R—NH_2} \longleftarrow$$

  Same type of reactions for aryl azides also.

- **Reduction of acid amide :**

  $$\underset{\substack{|\\ NH_2}}{R—\overset{\overset{O}{||}}{C}} \xrightarrow{2[H]} \underset{\substack{|\\ NH_2\ (H)}}{R—\overset{\overset{O—H\,(H)}{|}}{C}—H} \xrightarrow[(-H_2O)]{2[H]} \underset{\text{(1° Amine)}}{R—CH_2—NH_2}$$

  (Reducible area)

  If N-substituted *i.e.*, *N*-alkyl amide is used then 2° amine is obtained.

  $$\underset{\substack{|\\ NHR_2}}{R—\overset{\overset{O}{||}}{C}} \xrightarrow[\text{steps}]{\text{All similar}} \underset{\text{(2° Amine)}}{R_1—CH_2—NHR_2}$$

A few common reducing agents are listed as follows :
- (i)   LiAlH$_4$ in ether
- (ii)   LiBH$_4$ in ether
- (iii) NaBH$_4$/AlCl$_3$
- (iv)   LiAlH$_4$/AlCl$_3$
- (v)   NaBH$_4$/PtCl$_2$
- (vi)   NaBH$_4$/alcohol
- (vii) B$_2$H$_6$/THF
- (viii) Red P/HI
- (ix)   Active metal + acid
  e.g., Zn + CH$_3$COOH, Sn + conc. HCl, Fe + HCl, Zn + HCl, etc.
- (x)   H$_2$ + Ni or Pt or Pd
- (xi)   H$_2$ + Pd — charcoal
- (xii) NaAlH$_4$
- (xiii) Alkali metal + alcohol
- (xiv) H$_2$, PtO$_2$ or Adam's catalyst

Lindlar's Catalyst

Lindlar's catalyst is used to reduce alkynes to alkenes. It does not easily reduce alkenes to alkanes. Lindlar's catalyst is used to stop the reaction at the alkene stage. This is why poisoning of the Lindlar's catalyst which is actually Pd/CaCO$_3$ is required. Poisoning is done in two ways :

- With lead : It lessens the activity of the catalyst.It is represented as Pd, CaCO$_3$, Pb(OAc)$_2$

- With BaSO$_4$/quinoline : This can also be used along with Pd/CaCO$_3$ to serve the purpose.

  Structure of quinoline is :

Question from students' mind

Q. What is the exact role of BaSO$_4$?

Ans: BaSO$_4$ along with CaCO$_3$ acts as a support to the reduced substances *i.e.*, it allows the reduced substance to escape from the catalyst. BaSO$_4$ also helps to stop over reduction and is a negative catalyst here.

- Remember that, Lindlar's catalyst also helps to convert $R—\overset{\overset{O}{||}}{C}—X$ to $R—\overset{\overset{O}{||}}{C}—H$.

Q. CH$_3$—CH=CH—CH$_2$—C≡C—CH$_2$—$\overset{\overset{||}{O}}{C}$—Cl

What is the product? $\xleftarrow{\text{Lindlar's catalyst}}$

Ans. CH$_3$—CH=CH—CH$_2$—CH=CH—CH$_2$—CHO

Addition of H$_2$ by Lindlar's catalyst is *syn* in nature.

H$_2$ + Ni or H$_2$ + Raney Ni

Use of Ni is very much prevalent. Sophisticated use of Ni can be done in the Raney nickel form. It is the finely divided form of nickel. Raney nickel is made from a nickel-aluminium alloy. At first, aluminium is dissolved in conc. NaOH solution. This leaves nickel in fine powder form and a little part of liberated H$_2$ is absorbed in nickel and can serve the reduction process. H$_2$/Ni reduces a number of reducible substances for example,

So, it is preferential reduction of benzene ring over —C— group.

$$\overset{\displaystyle -\underset{\underset{O}{\|}}{C}-}{}$$

H_2/Raney Ni or Ni reduces triple bond to double bond and then double bond to single bond. For example,

$$CH_3-C{\equiv}C-CH_3 \xrightarrow[\text{Raney Ni}]{H_2/} CH_3-CH{=}CH-CH_3$$

$$\xrightarrow{H_2/\text{Raney Ni}} CH_3-CH_2-CH_2-CH_3$$

H₂ + Pd + C (Charcoal)

In this, usually Pd is present 5% - 10% by mass and the rest is charcoal. In the $PdCl_2$ solution, charcoal is suspended and the $PdCl_2$ is reduced to Pd usually with H_2 or sometimes with formaldehyde (HCHO). Pd metal gets precipitated on charcoal and later this can be filtered and dried. Usually following reductions are carried out by H_2 + Pd + C :

(i)   Double bond (=) $\longrightarrow$ Single bond (—)
      (Triple bond is not involved).

(ii) $-NO_2 \longrightarrow -NH_2$

(iii) $-CN \longrightarrow -CH_2NH_2$

(iv) Azide $\longrightarrow$ 1° Amine

(v)

(vi) $-\underset{\underset{O}{\|}}{C}-$ is not touched by H_2 + Pd + C.

For example,

In the catalytic hydrogenation, first step is the chemical adsorption of H_2 on the metal surface. This causes the H—H bond breakage.

In the second step, the metal attaches to the double bond and hydrogen is transferred from the metal to the alkene.

H₂ + PtO₂, AcOH

PtO_2 or platinum oxide is known as Adam's catalyst. Here, PtO_2 gets reduced and actually Pt serves the purpose of a catalyst.

The following two examples will give an idea about the functional aspects of this reagent.

○

Preferential reduction of benzene takes place over —COOH or $-\underset{\underset{O}{\|}}{C}-$ group.

○

cis-product (82%)   trans-product (18%)

DIBAL-H

Full name of DIBAL-H is di-isobutyl aluminium hydride. Its molecular structure is

$$\left(CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2\right)_2 Al-H$$

Usually it is represented as

Al—H. A bridged form is also obtained.

Fundamental reductions preformed by DIBAL-H are :

○ Esters $\longrightarrow$ Aldehydes

$$MeOH + CH_3-CH_2-CH_2-CHO$$

○ Cyanide $\longrightarrow$ Aldehyde (in presence of HCl)
   (RCN)   (RCHO)

DIBAL-H does not reduce triple bond or double bond. E.J Corey, in his synthesis of prostaglandins, relied on DIBAL-H to convert lactone into lactols (cyclic hemiacetal.

Exact reaction is as follows :

$$RO \xrightarrow[-70°C]{\text{DIBAL-H}} \xleftrightarrow{H_2\ddot{O}}$$

(structures of lactone reduction with DIBAL-H shown)

○ Mechanism for conversion of ester to aldehydes using DIBAL-H is as follows :

$$\underset{R}{\overset{O}{\underset{|}{C}}}OEt \xrightarrow[\substack{-70°C \\ \text{Inert} \\ \text{solvent}}]{\text{DIBAL-H}} \overset{+}{\ddot{O}}-\bar{Al}\,i\text{-}Bu_2 \xrightarrow{\substack{\text{Hydride} \\ \text{transfer}}}$$

$$\xrightarrow[(-EtOH)]{H_2\ddot{O}:}$$

$$R-\underset{H}{\overset{\ddot{O}-Al\,i\text{-}Bu_2}{C}} \longrightarrow R-C-H \xrightarrow{-H_2O} RCHO$$

Look at the following example :

$$\text{CN} \xrightarrow[\substack{2.\ H_3O^+}]{\substack{1.\ \text{DIBAL-H,} \\ -70°C}} \text{CHO}$$

LiAlH₄

○ **Preparation :** In dry ether medium, a suitable amount of anhydrous $AlCl_3$ is added with the paste of LiH.

$$4LiH + AlCl_3 \xrightarrow{\text{dry ether}} Li[\overset{+}{\underset{}{\ddot{Al}H_4}}] + 3LiCl$$

○ **Working mechanism :** The following conversions are given by $LiAlH_4$:
  (i) Converts ester into alcohol.
  (ii) Reduces all types of $-\underset{||}{\overset{}{C}}-$ group $i.e.$,

$$R-\underset{O}{\overset{||}{C}}-R, \quad R-\underset{O}{\overset{||}{C}}-H, \quad R-\underset{O}{\overset{||}{C}}-Cl,$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$

$$R-\underset{OH}{\overset{|}{CH}}-R \qquad R-CH_2OH \qquad R-CHO$$

$$R-\underset{O}{\overset{||}{C}}-NH_2$$
$$\downarrow$$
$$R-CH_2NH_2$$

(iii) $-C\equiv N \longrightarrow -CH_2NH_2$

(iv) Doesn't reduce triple or double bond but if the double bond is in the conjugation with the benzene ring then it reduces the double bond. $i.e.$,

$$CH_3-CH=CH-CH_2-CHO$$
$$\downarrow LiAlH_4$$
$$CH_3-CH=CH-CH_2-CH_2OH$$

$$Ph-CH=CH-CHO \xrightarrow{LiAlH_4}$$
$$Ph-CH_2-CH_2-CH_2OH$$

$$4R-\underset{O}{\overset{||}{C}}-R' + LiAlH_4 \xrightarrow[\text{or THF}]{\text{Ether}} \left(R-\underset{R'}{\overset{H}{\underset{|}{C}}}-O\right)_4 \overset{+}{\ddot{Al}Li}$$

$$\downarrow HCl/H_2O$$

$$4R-\underset{R'}{\overset{}{\underset{|}{CH}}}-OH + AlCl_3 + LiCl$$

Excess of $LiAlH_4$ is destroyed with acid.

$$LiAlH_4 + 4HCl \longrightarrow LiCl + AlCl_3 + 4H_2$$

Mechanism can be shown as follows :

$$R-\underset{O}{\overset{R}{\underset{||}{C}}} + \left[\ddot{Al}H_3\right]Li^+ \longrightarrow [R_2CHO\ddot{Al}H_3]Li^+$$
$$\downarrow 3RCOR$$
$$4R_2CHOH + Li^+ + Al^{3+} \xleftarrow{H^+/H_2O} [(R_2CHO)_4\ddot{Al}]\overset{+}{Li}$$

Note down a very important thing.

$$R-\underset{O}{\overset{}{\underset{||}{C}}}-R \longrightarrow R-\underset{\underset{\textcircled{H}}{|}}{\overset{R}{\underset{|}{C}}}-O-\textcircled{H} \rightarrow \text{This comes from water}$$

This comes from $LiAlH_4$

Hence, in the reaction of carbonyl compounds, half of the hydrogen is supplied by $LiAlH_4$ and the other half from H_2O.

In the above example, out of four hydride transfers, the first one takes place very fast but subsequently with the increase in the number of alkoxy groups and their electron withdrawing nature rate of hydride transfer becomes slow.

LiBH$_4$

○ Lithium borohydride though apparently looks similar to lithium aluminium hydride but it is quite more chemoselective than LiAlH$_4$. Consider the following example :

$$\text{EtOOC} \diagdown \diagup \diagdown \text{COOH} \xrightarrow[\text{MeOH}]{\text{LiBH}_4}$$

$$\text{HO} \diagdown \diagup \diagdown \text{COOH}$$

So, ester is reduced over acid.
LiBH$_4$ also does not select (—COOH) over (—CONH$_2$) for reduction.

$$\text{EtOOC} \diagdown \diagup \text{CONH}_2 \xrightarrow[\text{MeOH}]{\text{LiBH}_4}$$

$$\text{HOH}_2\text{C} \diagdown \diagup \diagdown \text{CONH}_2$$

NaBH$_4$

○ **Preparation :** Though there are a lot of ways but mainly NaBH$_4$ is prepared by heating NaH with trimethoxy borane at a high temperature (250°C-300°C).

$$4\text{NaH} + \text{B}\overset{\text{OMe}}{\underset{\text{OMe}}{-\text{OMe}}} \xrightarrow{250°C\text{-}300°C} \text{NaBH}_4 + 3\text{MeONa}$$

Remember that NaBH$_4$ is soluble in water and alcohol but not in ether.

○ **Working mechanism :** Mechanistic approach is similar to that of LiAlH$_4$ but NaBH$_4$ acts slowly than LiAlH$_4$. Here, direct transfer of hydride does not take place at the very first step rather complexing of oxygen takes place.

$$R\text{—}\underset{\overset{\|}{O}}{\overset{..}{C}}\text{—}R + \overset{+}{\underset{H}{\ddot{B}H_3Na}} \longrightarrow R\text{—}\underset{R}{\overset{\overset{\delta^-}{O}..\overset{\delta^-}{\cdots}\overset{+}{BH_3Na}}{C}} \underset{H}{\curvearrowleft}$$

$$\left[R\text{—}\underset{R}{\overset{\overset{H}{|}}{\underset{|}{C}}}\text{—}\overset{..}{O} \right]_4 \overset{+}{\ddot{B}Na} \xleftarrow{3 \; RCOR} R\text{—}\underset{R}{\overset{|}{CH}}\text{—}O\text{—}\overset{..}{\ddot{B}}H_3\overset{+}{Na}$$

$$\xrightarrow{H_3O^+} 4\; R\underset{\overset{|}{OH}}{CHR} + H_3BO_3 + NaOH$$

○ **Common reaction aspects of NaBH$_4$**
(i) —CHO $\longrightarrow$ —CH$_2$OH
(ii) $>$C=O $\longrightarrow$ $>$CH—OH
(iii) $-\underset{\overset{\|}{O}}{C}\text{—Cl} \longrightarrow$ —CH$_2$OH

Remember that NaBH$_4$ does not reduce triple or double bond but the following observation says that some percentage of double bond gets reduced with NaBH$_4$.

$$\text{CH}_3\text{—CH}=\text{CH—CHO} \xrightarrow[\text{(2) H}_3\text{O}^+]{\text{(1) NaBH}_4/\text{alcohol}}$$

$$\underset{(60\%)}{\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}} + \underset{(40\%)}{\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}}$$
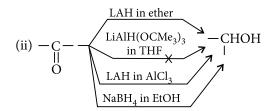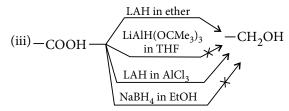
Consider the following reactions :

(i) —CHO
- LAH in ether → CH$_2$OH
- LiAlH(OCMe$_3$)$_3$ ✗→ CH$_2$OH
- LAH in AlCl$_3$ → CH$_2$OH
- NaBH$_4$ in EtOH → CH$_2$OH

(ii) $-\underset{\overset{\|}{O}}{C}-$
- LAH in ether → —CHOH
- LiAlH(OCMe$_3$)$_3$ in THF ✗→
- LAH in AlCl$_3$ →
- NaBH$_4$ in EtOH →

(iii) —COOH
- LAH in ether → —CH$_2$OH
- LiAlH(OCMe$_3$)$_3$ in THF ✗→
- LAH in AlCl$_3$ →
- NaBH$_4$ in EtOH ✗→

(iv) $-\underset{\overset{\|}{O}}{C}-\text{Cl}$
- LAH in ether → —CH$_2$OH
- LAH in AlCl$_3$ →
- NaBH$_4$ in EtOH →
- LiAlH(OCMe$_3$)$_3$ → $-\underset{\overset{\|}{O}}{C}-\text{H}$
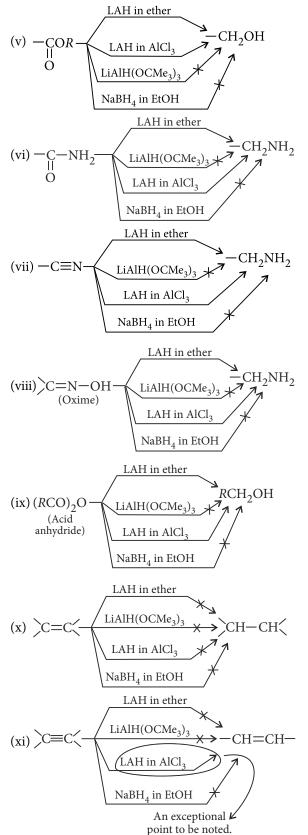
$$(v) \quad \underset{O}{\underset{\|}{-C}}OR \xrightarrow[\substack{\text{LAH in ether} \\ \text{LAH in AlCl}_3 \\ \text{LiAlH(OCMe}_3)_3 \\ \text{NaBH}_4 \text{ in EtOH}}]{} -CH_2OH$$

$$(vi) \quad \underset{O}{\underset{\|}{-C}}-NH_2 \xrightarrow[\substack{\text{LAH in ether} \\ \text{LiAlH(OCMe}_3)_3 \\ \text{LAH in AlCl}_3 \\ \text{NaBH}_4 \text{ in EtOH}}]{} -CH_2NH_2$$

$$(vii) \quad -C\equiv N \xrightarrow[\substack{\text{LAH in ether} \\ \text{LiAlH(OCMe}_3)_3 \\ \text{LAH in AlCl}_3 \\ \text{NaBH}_4 \text{ in EtOH}}]{} -CH_2NH_2$$

$$(viii) \quad \underset{\text{(Oxime)}}{>C=N-OH} \xrightarrow[\substack{\text{LAH in ether} \\ \text{LiAlH(OCMe}_3)_3 \\ \text{LAH in AlCl}_3 \\ \text{NaBH}_4 \text{ in EtOH}}]{} -CH_2NH_2$$

$$(ix) \quad \underset{\substack{\text{(Acid} \\ \text{anhydride)}}}{(RCO)_2O} \xrightarrow[\substack{\text{LAH in ether} \\ \text{LiAlH(OCMe}_3)_3 \\ \text{LAH in AlCl}_3 \\ \text{NaBH}_4 \text{ in EtOH}}]{} RCH_2OH$$

$$(x) \quad >C=C< \xrightarrow[\substack{\text{LAH in ether} \\ \text{LiAlH(OCMe}_3)_3 \\ \text{LAH in AlCl}_3 \\ \text{NaBH}_4 \text{ in EtOH}}]{} >CH-CH<$$

$$(xi) \quad >C\equiv C< \xrightarrow[\substack{\text{LAH in ether} \\ \text{LiAlH(OCMe}_3)_3 \\ \text{LAH in AlCl}_3 \\ \text{NaBH}_4 \text{ in EtOH}}]{} -CH=CH-$$

An exceptional point to be noted.
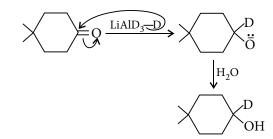
NaAlH$_4$

Preparational aspects are similar as discussed in earlier cases. Its use is specially done in conversion of ester to aldehyde and alcohol. (Note : not acid and alcohol).

$$RCOO\{R' \xrightarrow{\text{NaAlH}_4} RCHO + R'OH$$

break after —COO

LiAD$_4$

○ Used to insert deuterium wherever necessary. For example,

CHEMISTRY MUSING

1. **(d):** The fact that the carvone enantiomers smell differently is due to the fact that the receptor sites in the nose are chiral, and only the correct enantiomer will fit its particular site (just as a hand requires a glove of the correct chirality for a proper fit).

2. **(c):** $N \equiv N + \dfrac{1}{2} O = O \longrightarrow N = N = O$
$$\Delta H_f^\circ = 82 \text{ kJ mol}^{-1}$$

$\therefore$ $\Delta H_{reaction}$ = [Sum of the bond energies of reactants – Sum of the bond energies of products]

$= [1 \times N \equiv N + \dfrac{1}{2} \times O = O]$
$\quad - [1 \times N = N + 1 \times N = O]$

$= [1 \times 946 + \dfrac{1}{2} \times 498] - [1 \times 418 + 1 \times 607]$

$= 1195 - 1025 = 170 \text{ kJ mol}^{-1}$

$\therefore$ Resonance energy of N_2O =
Experimental $\Delta H_{f(N_2O)}$ – Calculated $\Delta H_{f(N_2O)}$

$= 82 - 170 = -88 \text{ kJ mol}^{-1}$

3. **(a):** Groups having $+I$ effect increases the basicity and $-I$ effect decreases the basicity. C-2 is joined with two methyl groups whereas C-5 is joined with one ethyl group. Hence, OH at C-2 is more basic than OH at C-5.

4. **(c):** Moles of Cl^- ions ionised from moles of $CrCl_3 \cdot 6H_2O = \dfrac{2.665}{266.5} = 0.01$

$\therefore$ Moles of AgCl obtained = Moles of Cl^- ionised

$= \dfrac{2.87}{143.5} = 0.02$

Thus, 0.01 mole of complex $CrCl_3 \cdot 6H_2O$ gives 0.02 mole of Cl^- on ionisation.

Now, since coordination number of Cr is six and only one Cl^- ion is attached to Cr by coordinate bond or secondary valency and therefore, complex is $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$.

$[CrCl(H_2O)_5]Cl_2 \cdot H_2O \longrightarrow [CrCl(H_2O)_5]^{2+} + 2Cl^- + H_2O$

$2Cl^- + 2AgNO_3 \longrightarrow 2AgCl + 2NO_3^-$

5. **(c):** Glycol blocks the carbonyl group.

$CH_3-C-CH_2-C\equiv CH \xrightarrow{NaNH_2/CH_3I}$

(structures with glycol-protected ketone)

$\xrightarrow{H^+} CH_3-C-CH_2-C\equiv C-CH_3$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-C\equiv C-CH_3$

6. **(c):** Removal of γ-hydrogen of crotonaldehyde provides more stable allylic carbanion, hence here γ-carbon (not α) provides the carbanion (nucleophile) for carbonyl carbon of cinnamaldehyde.

$H_2C-CH=CH-C=O \xrightarrow{OH^-}$

$H_2C=CH-CH=C-O^-$

7. **(b):** X_2 is O_2, X_3 is O_3 and Y_2 is I_2.
$2I^- + H_2O + O_3 \longrightarrow 2OH^- + I_2 + O_2$

8. **(d):** $I_2 + \underset{Excess}{I^-} \longrightarrow$ Brown coloured I_3^- ion
I_2 + Starch = Blue colouration
O_2 is thermodynamically more stable as compared to O_3.
O_3 is a pale-blue gas having characteristic smell.

9. **(5):** $K.E. = \dfrac{1}{2}mu^2 = 5.2 \times 10^{-21} \Rightarrow u = 2491 \text{ m/s}$

and thus, time taken to travel 100 m distance is

$t = \dfrac{100}{2491} = 0.04 \text{ second}$

Also, $\dfrac{dN}{dt} = \lambda.N$ or $\dfrac{dN}{N} = \lambda.dt$

$= \dfrac{0.693}{t_{1/2}} \times dt = \dfrac{0.693}{700} \times 0.04 = 3.96 \times 10^{-5}$

10. **(6):** Doping of $SrCl_2$ to NaCl brings in the replacement of two Na^+ ions by each Sr^{2+} ion, but each Sr^{2+} ion occupies only one lattice point. This produces a cation vacancy.

Thus, doping of 10^{-3} mole of $SrCl_2$ in 100 moles of NaCl will produce cation vacancies = 10^{-3}

100 moles of NaCl will have cation vacancies after doping = 10^{-3}

$\therefore$ Cation vacancies in 1 mole NaCl $= \dfrac{10^{-3}}{100} = 10^{-5}$

$\therefore$ Total cationic vacancies $= 10^{-5} \times N_A$
$= 6.02 \times 10^{18} \simeq 6 \times 10^{18}$

◆◆

Solution Senders of Chemistry Musing
SET 30

1. Yakaiah Chennori (Warangal)
2. Naresh Polam (Andhra Pradesh)
3. Chakravarthy Kalyan (Telangana)
4. Sayak Mandal (West Bengal)
5. AVN Prasad (Assam)
6. Mabu Shaik

Hydrogen and its Compounds

- Hydrogen is the first element in the periodic table.
- Electronic configuration is $1s^1$.
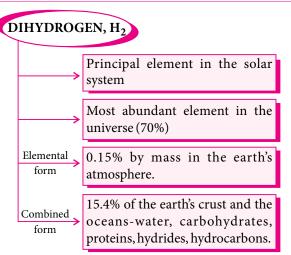- It resembles with both metals and halogens to a certain extent.

Resemblance with Alkali metals	Resemblance with Halogens
- Similar outer electronic configuration : ns^1. - Lose one electron to form unipositive ions. - Form oxides, halides, and sulphides.	- Short by one electron to the corresponding noble gas configuration. - Gain one electron to form uninegative ions. - High ionization enthalpies. - Form diatomic molecules. - Combine with other elements to form hydrides and a large number of covalent compounds.

Position in the periodic table

- Hydrogen is placed in no specific group due to its property of gaining electron (when H^- is formed) and also losing electron (when H^+ is formed).
- In the view of the anomalous behaviour of hydrogen it is difficult to assign any definite position to it in the periodic table. Hence it is customary to place it in group 1 as well as in group 17. But yet its position is uncertain.
- **Isotopes of hydrogen :** 3 isotopes : Protium ($_1^1H$), Deuterium ($_1^2H$ or D), Tritium ($_1^3H$ or T).
  - The isotopes have different physical properties (due to large difference in their masses) but similar chemical properties (except the rates of reactions due to different bond dissociation enthalpy).
  - Only tritium is radioactive and emits β^- particles.

DISCOVERY AND OCCURRENCE

- Hydrogen was prepared by Henry Cavendish in 1766 by the action of acids on metals. It was named "inflammable air." Lavoisier named it hydrogen (hydra = water, gennas = maker) meaning water maker.
- In the elemental form, hydrogen exists as diatomic molecule (H_2), called dihydrogen.

DIHYDROGEN, H_2

Elemental form:
- Principal element in the solar system
- Most abundant element in the universe (70%)
- 0.15% by mass in the earth's atmosphere.

Combined form:
- 15.4% of the earth's crust and the oceans-water, carbohydrates, proteins, hydrides, hydrocarbons.

Laboratory preparation

- **From acids and alkaline earth metals, Zn, Mg, Fe, etc.**

  $e.g.,$ $\underset{\text{(Granulated)}}{Zn}$ + $\underset{\text{(Dil.)}}{2HCl}$ $\longrightarrow ZnCl_2 + H_2\uparrow$

- **From alkalies and Zn, Al, Sn (amphoteric metals).**

  $e.g.,$ $Zn + 2NaOH_{(aq)} \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2}$ + $H_2\uparrow$

- **From water and active metals**

  (a) Active metals like Na, K react at room temperature.

  $2Na + \underset{\text{(Cold)}}{2H_2O} \longrightarrow 2NaOH + \underset{\text{(Violent)}}{H_2}\uparrow$

(b) Less active metals like Zn, Mg, Al, liberate hydrogen only on heating.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2\uparrow$$
(Hot)

(c) Metals like Fe, Co, Ni, Sn can react only by passing steam.

$$\underset{\text{(Red hot)}}{3Fe} + \underset{\text{(Steam)}}{4H_2O} \longrightarrow \underset{\text{(Magnetic oxide)}}{Fe_3O_4} + 4H_2\uparrow$$

❑ **Uyeno's method :** Very pure hydrogen is obtained with rapidity by the action of caustic potash on scrap aluminium. This method is used for military purposes.

$$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2\uparrow$$

Commercial production

❑ By electrolysis of acidified water using platinum electrodes.

$$2H_2O_{(l)} \xrightarrow[\text{traces of acid or base}]{\text{Electrolysis}} 2H_{2(g)} + O_{2(g)}$$

❑ By the reaction of steam on hydrocarbons at high temperatures.

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Ni}]{1270\ K} \underbrace{nCO + (2n + 1)H_2}_{\text{Water gas}}$$

Water gas also called as synthesis gas or syn gas as it is used in the synthesis of methanol and a large number of hydrocarbons.

❑ As a by-product in the manufacture of NaOH and Cl_2 by electrolysis of brine solution.

At anode : $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$

At cathode : $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

Physical properties

❑ It is colourless, odourless, tasteless, combustible gas, lighter than air, insoluble (or slightly soluble) in water, lightest, diatomic, has low melting and boiling points.

Chemical properties

❑ H_2 is relatively inert at room temperature due to high H–H bond enthalpy.

❑ Undergoes chemical reactions by either of the following ways :
  (i) Losing the electron form H^+ ion.
  (ii) Gaining an electron to form H^- ion.
  (iii) Sharing electrons to form a single covalent bond.

❑ Reacts with halogens to give halides.
  $H_{2(g)} + X_{2(g)} \rightarrow 2HX_{(g)}$ $(X = F, Cl, Br, I)$
  H_2 reacts with F_2 in dark also, but with I_2 only in the presence of catalyst.

❑ Reacts with dioxygen to form water with evolution of heat.

$$2H_{2(g)} + O_{2(g)} \xrightarrow{\Delta\ \text{or catalyst}} 2H_2O_{(g)}$$

❑ Reaction with dinitrogen to form ammonia (Haber's process)

$$3H_{2(g)} + N_{2(g)} \xrightarrow[\text{Fe}]{673\ K,\ 200\ atm} 2NH_{3(g)};$$
$$\Delta H^\circ = -92.6\ kJ\ mol^{-1}$$

❑ Reacts with many metals at high temperature to give hydrides.
  $H_{2(g)} + 2M_{(g)} \longrightarrow 2MH_{(s)}$ $(M = \text{alkali metal})$

❑ Reduces some metal ions in aqueous solution.
  $H_{2(g)} + Pd^{2+}_{(aq)} \longrightarrow Pd_{(s)} + 2H^+_{(aq)}$

❑ Reduces oxides of some metals less reactive than iron to corresponding metals.
  $yH_{2(g)} + M_xO_{y(s)} \longrightarrow xM_{(s)} + yH_2O_{(l)}$

❑ Reactions with organic compounds :
  ○ Hydrogenation of vegetable oils in the presence of nickel as a catalyst to give edible fats such as margarine and vanaspati ghee.
  ○ Hydroformylation of olefins (alkenes) to give aldehydes and then alcohols.

$$H_2 + CO + \underset{\text{Olefin}}{RCH=CH_2} \xrightarrow[\text{High temp., pressure}]{[Co(CO)_4]_2}$$
$$\underset{\text{Alcohol}}{RCH_2CH_2CH_2OH} \xleftarrow[\text{Ni}]{H_2} \underset{\text{Aldehyde}}{RCH_2CH_2CHO}$$

Uses

❑ Used in the manufacture of ammonia, methanol, vanaspati fat by hydrogenation of vanaspati oils, metal hydrides, hydrogen chloride.

❑ Used to reduce metal oxides to metals in metallurgical processes.

❑ Used as a rocket fuel in fuel cells to generate electricity.

❑ Used in atomic hydrogen and oxy-hydrogen torches, which are used in cutting and welding purposes. Atomic hydrogen atoms recombine with the surface to be welded to raise the temperature to 4000 K.

Dihydrogen does not produce pollution and has more fuel efficiency than gasoline and other fuels. The only pollutants are oxides of nitrogen (due to presence of dinitrogen as impurity). Pollutants can be minimized by injection of small amount of water into the cylinder to lower the temperature. As a result, dinitrogen will not react with dioxygen.

HYDRIDES

- Hydrogen forms binary compounds called hydrides with other elements except noble gases.

  eg., EH_x (E - element)

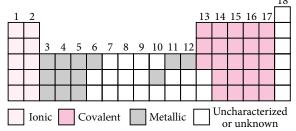 In hydrides, oxidation state of hydrogen = -1

- **Classification :** 3 types

Fig.: The different classes of binary hydrogen compounds and their distribution in the periodic table

- **Ionic or Saline or Salt-like Hydrides**
  - They are stoichiometric compounds of hydrogen with highly electropositive s-block elements.
  - **Exception :** Lighter metal hydrides such as LiH, BeH_2, MgH_2 are covalent in nature.
  - They are crystalline, non-volatile, non-conducting in solid state, but conducting in molten state.
  - On electrolysis, liberate H_2 gas at anode.

    $$2H^- \text{ (melt)} \xrightarrow{\text{Anode}} H_{2(g)} + 2e^-$$
  - React violently with water to produce dihydrogen gas.

    $$NaH_{(s)} + H_2O_{(aq)} \longrightarrow NaOH_{(aq)} + H_{2(g)}$$
  - Lithium hydride is used in the synthesis of some useful hydrides as lithium hydride does not react with oxygen and chlorine at moderate temperature.

    $$8LiH + Al_2Cl_6 \xrightarrow{\text{Dry ether}} 2LiAlH_4 + 6LiCl$$
    $$2LiH + B_2H_6 \xrightarrow{\text{Dry ether}} 2LiBH_4$$

- **Covalent or Molecular Hydrides**
  - They are compounds of hydrogen with *p*-block elements such as CH_4, NH_3, H_2O, HF, etc.
  - Further classified into three categories on the basis of the relative numbers of electrons and bonds in their Lewis structure.
  - **Electron-deficient hydrides :** formed by all group 13 elements. Have few electrons to write their conventional Lewis structure.

- **Electron-precise hydrides :** Formed by all group-14 elements. They are tetrahedral in shape and have as many numbers of electrons as required to write their conventional Lewis structure.

- **Electron-rich hydrides :** Formed by elements of group 15-17. They have excess electrons present as lone pairs and act as Lewis bases (electron donors).

- They undergo intermolecular H-bonding as a result of lone pairs of electrons on highly electronegative atoms such as N, O, and F. This leads to association of molecules and hence, there is an increase in boiling point. Higher the electronegativity, stronger is the H-bond and hence, higher is the boiling point.

Examples :

Compounds	Number of lone pairs
NH_3	1
H_2O	2
HF	3

- **Metallic or Non-stoichiometric or Interstitial Hydrides**
  - These are non-stoichiometric compounds formed by hydrogen with many *d*-block and *f*-block elements (except group 7, 8 and 9 and only Cr of group 6).
  - They conduct heat and electricity. They are called interstitial hydrides as it was thought that in these compounds, hydrogen occupies interstitial sites in the metal lattice without changing the type of the lattice. However later, it was found that the lattices of these hydrides are different from their metal lattices (exception– Ni, Pd, Ce and Ac).

The transition metals which can absorb hydrogen are used as catalysts in reduction hydrogenation reactions.

Some metals such as Pd, Pt are used as storage media of hydrogen as they can accommodate a large volume of hydrogen.

This property has a high potential for hydrogen storage and thus, these metals act as a source of energy.
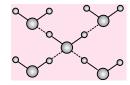
WATER

❑ Water is essential to all forms of life but distribution of water over the earth's surface is not uniform. Human body has about 65% water while some plants have as high as 95% water. Water is found in all three phases, *i.e.* solid, liquid and gas.

Physical properties

❑ It is bad conductor of electricity due to very low degree of ionisation.

❑ **Consequences of extensive H-bonding in water :** High freezing point, high boiling point, high heat of vaporization, high heat of fusion.

❑ **Water has the following properties higher than other liquids :** Specific heat, thermal conductivity, surface tension, dipole moment, dielectric constant.

❑ Water is a very good solvent for polar and ionic substances due to its polar character. It dissolves alcohols and carbohydrates due to H-bonding.

Structure

❑ In liquid state, water molecules are associated together by undergoing intermolecular H-bonding

❑ **Structure of ice :**

Why is ice slippery?
At temperatures as low as 200 K, the surface of ice is highly disordered and water-like. As the temperature approaches the freezing point, this region of disorder extends farther down from the surface and acts as a lubricant.

❑ Water crystallises in hexagonal form at atmospheric pressure and in cubic form at lower temperature.

❑ The structure of ice is highly ordered three-dimensional. According to X-ray study of ice crystals– each oxygen atom is tetrahedrally surrounded by four other oxygen atoms at 276 pm distance.

Water is denser than ice so it floats on water. In winter season, the ice formed resides on the surface of a lake. The ice on the surface water provides thermal insulation (heat does not pass from water to surroundings).

Chemical properties

❑ Water is amphoteric in nature (acts both as acid and base).

e.g., acts as an acid with NH_3 while as base with H_2S (Bronsted concept).

$H_2O_{(l)} + NH_{3(aq)} \longleftrightarrow OH^-_{(aq)} + NH_4^+_{(aq)}$
$H_2O_{(l)} + H_2S_{(aq)} \longleftrightarrow H_3O^+_{(aq)} + HS^-_{(aq)}$

Auto-protolysis (self-ionization) of water :

$e.g., \underset{\text{acid-1}}{H_2O_{(l)}} + \underset{\text{base-2}}{H_2O_{(l)}} \longleftrightarrow \underset{\substack{\text{acid-2} \\ \text{(conjugate acid)}}}{H_3O^+_{(aq)}} + \underset{\substack{\text{base-1} \\ \text{(conjugate base)}}}{OH^-_{(aq)}}$

❑ **Redox reactions**

○ Reduced to dihydrogen by highly electropositive metal.
$2H_2O_{(l)} + 2Na_{(s)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$

○ Oxidized to O_2 during photosynthesis and also with fluorine.
$6CO_{2(g)} + 12H_2O_{(l)} \rightarrow C_6H_{12}O_{6(aq)} + 6H_2O_{(l)} + 6O_{2(g)}$

$2F_{2(g)} + 2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + 4F^-_{(aq)} + O_{2(g)}$

○ Many ionic compounds and certain covalent compounds are hydrolysed in water.
$N^{3-}_{(s)} + 3H_2O_{(l)} \rightarrow NH_{3(g)} + 3OH^-_{(aq)}$
$P_4O_{10(s)} + 6H_2O_{(l)} \rightarrow 4H_3PO_{4(aq)}$
$SiCl_{4(l)} + 2H_2O_{(l)} \rightarrow SiO_{2(s)} + 4HCl_{(aq)}$

EXAM DATES 2016

JEE Main	:	3rd April (offline), 9th & 10th April (online)
VITEEE	:	6th to 17th April
MGIMS	:	17th April
Kerala PET	:	25th & 26th April
Kerala PMT	:	27th & 28th April
AIPMT	:	1st May
Karnataka CET	:	4th & 5th May
WBJEE	:	17th May
JEE Advanced	:	22nd May
AIIMS	:	29th May

○ Hydrates are formed during crystallization of some salts from aqueous solution. Types of association of water are tabulated as follows :

Coordinated water	Interstitial water	Hydrogen bonded water
$[Cr(H_2O)_6]^{3+}$ $3Cl^-$	$BaCl_2 \cdot 2H_2O$	$[Cu(H_2O)_4]^{2+}SO_4^{2-} \cdot H_2O$ in $CuSO_4 \cdot 5H_2O$

Only one molecule of water (outside the bracket *i.e.*, the coordination sphere) is hydrogen bonded in $CuSO_4 \cdot 5H_2O$. The other four molecules of water (inside the bracket) are coordinated.

Types of hardness

	Temporary hardness	Permanent hardness
Cause	Presence of magnesium and calcium bicarbonates.	Presence of soluble salts of magnesium and calcium as chlorides and sulphates.
Methods of removal	(i) Hard $H_2O \xrightarrow{\Delta}$ ppt $\xrightarrow{\text{Filtration}}$ Soft H_2O $Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2\downarrow + 2CO_2\uparrow$ $Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$ (ii) Clark's method Hard $H_2O \xrightarrow[\text{lime}]{\text{Addition of}}$ ppt $\xrightarrow{\text{Filtration}}$ Soft H_2O $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$ $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow$ $\qquad\qquad\qquad\qquad + Mg(OH)_2\downarrow + 2H_2O$	(i) Hard $H_2O \xrightarrow{Na_2CO_3}$ ppt $\xrightarrow{\text{Filtration}}$ Soft H_2O $MCl_2 + Na_2CO_3 \rightarrow MCO_3\downarrow + 2NaCl$ $MSO_4 + Na_2CO_3 \rightarrow MCO_3\downarrow + Na_2SO_4$ $\qquad\qquad\qquad\qquad\qquad (M=Mg, Ca)$ (ii) Calgon's method $Na_6P_6O_{18} \rightarrow 2Na^+ + Na_4P_6O_{18}^{2-}$ $M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$ (iii) Ion-exchange method [Zeolite/permutit ($NaAlSiO_4$ or NaZ) process] $2NaZ_{(s)} + M^{2+}_{(aq)} \rightarrow MZ_{2(s)} + 2Na^+_{(aq)}$

Soft water
❑ Soft water is free from soluble salts of Ca and Mg and it gives lather with soap easily.

Heavy water (D_2O)
❑ Heavy water was discovered by Harold clayton Urey, an American chemist. He showed that ordinary water contains traces (1 part in 6000 parts) of D_2O.

Preparation
❑ By exhaustive electrolysis of water.
❑ As a by-product in some fertilizer industries.

Uses
❑ As a moderater in nuclear reactors.
❑ In exchange reactions for the study of reaction mechanisms.
❑ In the preparation of deuterium compounds.

HARD AND SOFT WATER
Hard water
❑ Contains calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate.
It does not give lather with soap, instead forms scum/precipitate with it.

$2C_{17}H_{35}COONa_{(aq)} + M^{2+}_{(aq)} \rightarrow (C_{17}H_{35}COO)_2M +$
Sodium stearate (soap)   Precipitate
$\qquad\qquad 2Na^+_{(aq)} \ (M = Ca, Mg)$

That is why, it is not effective in washing and is harmful for boilers as salts are deposited in the form of scale which causes reduction of efficiency of the boiler.

HYDROGEN PEROXIDE (H_2O_2)
❑ Hydrogen peroxide was discovered by the French chemist, L.J. Thenard, in 1818, by the action of sulphuric acid on barium peroxide. It was called oxygenated water.

Preparation
❑ $BaO_2 \cdot 8H_2O_{(s)} + H_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + H_2O_{2(aq)}$
$\qquad\qquad\qquad\qquad\qquad + 8H_2O_{(l)}$

- Electrolytic oxidation of acidified sulphate solution :

$$2HSO_{4(aq)}^{-} \xrightarrow{\text{Electrolysis}} \underset{\text{Peroxodisulphate}}{HO_3SOOSO_3H_{(aq)}}$$

$$\xrightarrow{\text{Hydrolysis}} 2HSO_{4(aq)}^{-} + 2H_{(aq)}^{+} + H_2O_{2(aq)}$$
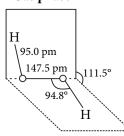
This method is also used in laboratory preparation of D_2O_2.
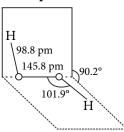
- **Industrial preparation**

  2-ethylanthraquinol $\xrightarrow[H_2/Pd]{O_2(air)} H_2O_2$ + Oxidised product

Structure : non planar

Gas phase

H
95.0 pm
147.5 pm   111.5°
94.8°
H

Dihedral angle is 111.5°

Solid phase

H
98.8 pm
145.8 pm   90.2°
101.9°
H

Dihedral angle is 90.2°

Physical properties

- It is miscible with water and forms a hydrate $H_2O_2 \cdot H_2O$.

- 30% solution of H_2O is marketed as '100 volume peroxide' (perhydrol). This means 1 L of H_2O_2 will give 100 L of oxygen at STP.

  Commercially, H_2O_2 is marketed as '10 volume'. This means it contains 3% H_2O_2.

Chemical properties

- H_2O_2 acts as both oxidising and reducing agent in both acidic and alkaline medium.

- **Oxidising agent**
  - In acidic medium
    $$2Fe_{(aq)}^{2+} + 2H_{(aq)}^{+} + H_2O_{2(aq)} \longrightarrow 2Fe_{(aq)}^{3+} + 2H_2O_{(l)}$$
    $$PbS_{(s)} + 4H_2O_{2(aq)} \longrightarrow PbSO_{4(s)} + 4H_2O_{(l)}$$
  - In basic medium
    $$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$$
    $$Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^-$$

- **Reducing agent**
  - In acidic medium
    $$2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$
    $$HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$$
  - In basic medium
    $$I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$$
    $$2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$$

H_2O_2 is stored in wax-lined glass or plastic vessels in dark because it slowly decomposes when exposed to light.

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

It is kept away from dust because dust can induce explosive decomposition of H_2O_2.

Urea is added as a stablizer.

Uses

Industry	Application
Pulp and paper	Bleaching wood pulp
Mining	Detoxification of cyanide tailings
Textile bleaching	Bleaching of cotton fabrics
Wool scouring	Bleaching of wool
Waste water treatment	Destroying soluble cyanides, sulphides and phenols
Packaging	Aseptic packaging of milk and fruit juice
Manufacturing	Hydroquinone, sodium perborate, percarbonate, pharmaceuticals (cephalosoporin), food products (like tartaric acid).

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ADVANCED CHEMISTRY BLOC

(THERMODYNAMIC EFFICIENCY OF FUEL CELL AND TEMPERATURE COEFFICIENT OF CELL)

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ELECTRICAL WORK AND FREE ENERGY

The work that is accomplished when electrons are transferred through a wire depends on the 'push' behind the electrons. This driving force is defined in terms of potential difference (in volts). Volt represents joule of work per coulomb of charge transfer.

$$\text{Potential difference (V)} = \frac{\text{Work (J)}}{\text{Charge (C)}}$$

Thus, 1 joule of work is obtained when 1 coulomb charge is transferred between two points having a potential difference of 1 volt.

Since the cell is used to run a motor, it means the work is done by the cell. Work flowing out of the system has a negative sign.

$$E = \frac{-w}{q} \text{ where, } q \text{ is } nF.$$

So, $w = -nFE$.

From thermodynamics, it is known that useful work (non-PV work like electrical work) corresponds to decrease in free energy. This electrical work thus can also be written as :

$$\Delta G = -w$$

EFFICIENCY OF CELL

When the emf corresponds to maximum cell potential, the work calculated will be the maximum work. It is known that the maximum cell potential is measured under 'no current' condition. However to obtain work, current must flow. When current flows some energy is inevitably wasted through frictional heating and the maximum work is not obtained. In any real, spontaneous process some energy is always wasted and the actual realised work is less than the calculated maximum.

Although it can never actually realise the maximum work for a cell reaction, the value for it is still useful in evaluating the efficiency of a real process based on the cell reaction. For example, suppose a certain Galvanic cell has maximum potential (at zero current) of 2.5 V and in a particular experiment, 1.33 moles of electrons were passed through a cell at an average actual potential of 2.1 V .Then the work obtained is calculated using the following formula :

$$w = -nFE$$

$$= -1.33 \text{ mole of } e^- \times 96,485 \frac{\text{coulomb}}{\text{mole of } e^-} \times 2.1 \text{ volt}$$

$$= -2.69 \times 10^5 \text{ joule}$$

For the maximum work, the maximum potential can be used and then,

$$w_{\max} = -nFE_{\max}$$

$$= 1.33 \text{ mole of } e^- \times 96,485 \frac{\text{coulomb}}{\text{mole of } e^-} \times 2.5 \text{ volt}$$

$$= -3.21 \times 10^5 \text{ joule}$$

Thus, in actual operation, the efficiency of this cell is

$$\frac{w}{w_{\max}} \times 100\% = \frac{-2.69 \times 10^5}{-3.21 \times 10^5} \times 100\% = 83.8\%$$

Efficiency of fuel cell

A fuel cell is an electrochemical cell where a combustion reaction becomes a cell reaction. For a fuel cell, efficiency is defined as the ratio between the work done by the cell and the enthalpy change of the cell reaction.

$$\text{Thermodynamic efficiency} = \frac{\Delta G}{\Delta H}$$

$$= \frac{\Delta H - T\Delta S}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H(-\text{ve})}$$

Since enthalpy of combustion is always negative, the sign and magnitude of ΔS determine the thermodynamic efficiency of fuel cell. The sign of ΔS in turn depends on the difference between the number of moles of gaseous products and reactants. This implies thermodynamic

efficiency of fuel cell depends on temperature. In fact, three situations may arise :

○ If the entropy change is quite small there is almost no variation of thermodynamic efficiency with temperature.

○ If the entropy change is significant and positive, thermodynamic efficiency would increase with temperature.

○ If the entropy change is significant and negative, thermodynamic efficiency would decrease with temperature.

Consider, hydrogen-oxygen fuel cell :

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$$

1.5 moles of gaseous reactants are consumed without releasing any gas. This corresponds to decrease in entropy of the system. Even if the product is gaseous, which is most likely under the conditions, still there is decrease in entropy. Sign of entropy change is negative and thermodynamic efficiency decreases with temperature.

Now consider direct methane fuel cell :

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Three moles of gases are consumed and three moles of gases are produced. So, there is no change in entropy and the maximum thermodynamic efficiency will be invariant of temperature.

Now consider another fuel cell where liquid formic acid is the fuel :

$$HCOOH_{(l)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(g)}$$

This time more gases are produced than consumed. So, sign of ΔS is positive and maximum thermodynamic efficiency will increase with increase in temperature. Theoretically, if temperature is taken to very high value, the maximum thermodynamic efficiency will go beyond even '1'. But this is never possible and practically, thermodynamic efficiency of fuel cell varies between 0.5 to 0.8.

Temperature coefficient of a cell

For thermodynamics, it can be proved that :

$$\left[\frac{\partial (\Delta G)}{\partial T} \right]_P = -\Delta S$$

The Gibbs' equation can now be written as :

$$\Delta G = \Delta H - T\Delta S = \Delta H + T\left[\frac{\partial (\Delta G)}{\partial T} \right]_P$$

or, $$-\Delta G = -\Delta H - T\left[\frac{\partial (\Delta G)}{\partial T} \right]_P$$

Where, $-\Delta H$ is equal to the decrease in enthalpy of the cell reaction at constant pressure. On putting the value of $\Delta G = -nFE$, the above equation modifies to

$$nFE = -\Delta H - T\left[\frac{\partial (-nFE)}{\partial T} \right]_P$$

or, $$nFE = -\Delta H + nFT\left[\frac{\partial E}{\partial T} \right]_P$$

or, $$E = -\frac{\Delta H}{nF} + T\left[\frac{\partial E}{\partial T} \right]_P$$

As is clear from the second last equation, nFE is equal to or greater or lesser than the enthalpy of the cell reaction. The exact nature depends on the sign of the term $\left[\frac{\partial E}{\partial T} \right]_P$, which is called the temperature coefficient of the cell.

○ When temperature coefficient of cell is zero, the electrical energy of the cell is equal to enthalpy of the reaction.

○ If it is positive, the emf of the cell increases with increase in temperature. The electrical energy will be greater than the enthalpy of the cell reaction. The additional energy will be supplied to the cell from the surroundings and if it is not possible, the temperature of the cell falls during working.

○ If it is negative, the electrical energy will be less than the enthalpy of the cell reaction. The difference will be given out to surroundings. If this is not possible, temperature of the cell rises during working.
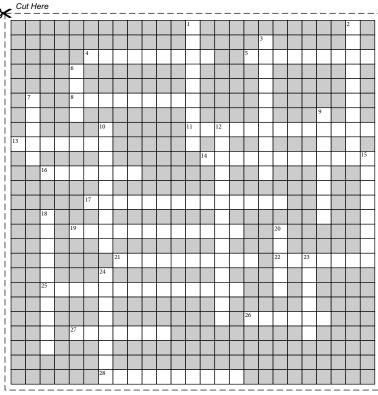
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CROSS WORD

ACROSS

4. The main structural unit of the cell walls of plants. (9)
5. The mass of one mole of a substance in grams. (9)
8. Interconvertible keto and enol forms. (9)
11. Substances which change colour with temperature. (13)
13. The quantity of heat required to raise the temperature of one gram of water through 1°C. (7)
14. The temperature at which an equilibrium exists between well ordered crystalline state and the more random liquid state. (12)
16. Cyclic amides. (7)
17. The quantitative relationships between electricity and chemical change were first described by. (14)
19. A technique concerned with the investigation of spectra produced when matter interacts with or emits electromagnetic radiation. (12)
21. A glass containing lead silicate which is used for optical instruments. (10)
22. Boron hydrides are also called. (7)
25. The reaction of cleavage of a chemical bond by hydrogen. (14)
26. A complex that can exchange ligands at a rapid rate. (6)
27. A dark brown pigment of hair, eyes and skin. (7)
28. The maximum amount of the solute in grams which can dissolve in 100 g of the solvent to form a saturated solution at that particular temperature. (10)

DOWN

1. The internal resistance to flow possessed by a liquid. (9)
2. The process of separation of racemates into their component enantiomers. (10)
3. Acids which contain more than one acidic hydrogen per molecule. (10)
6. Radiations emitted from the nucleus when a neutron is converted into a proton, an electron and a neutrino. (4)
7. A series of lines in the ultraviolet spectrum emitted by excited hydrogen atoms. (5)
9. An ore containing carbonates of Mg and Ca. (8)
10. A class of drugs that is used for reducing nervousness and excitement. (9)
12. The process involving the coating of a solid surface with a metal layer by the application of electrolysis. (14)
15. Organic polysulphide polymers. (8)
18. Element used in fertilizers which is responsible for root growth. (10)
20. Crystal system to which diamond belongs. (5)
23. The crystalline form of TiO_2 where Ti is surrounded octahedrally by six O atoms. (6)
24. Members of a homologous series. (8)

Cut Here